



Digitized by the Internet Archive
in 2008 with funding from
Microsoft Corporation

668

THE CHEMICAL NEWS, JULY 15, 1904.

THE
CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXXIX.—1904

40667
17/10/06

LONDON:

PUBLISHED AT THE OFFICE, 16, NEWCASTLE STREET, FARRINGDON ST.,
E.C.

AND SOLD BY ALL BOOKSELLERS.

MDCCCIV.

CHEMICAL NEWS,
July 15, 1904.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,
16, NEWCASTLE STREET, FARRINGTON STREET,
E.C.

THE CHEMICAL NEWS.

VOLUME LXXXIX.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2301.—JANUARY 1, 1904.

THE ACTION OF RADIIUM, RÖNTGEN RAYS, AND ULTRA-VIOLET LIGHT ON MINERALS.*

By GEORGE F. KUNZ, Ph.D. A.M.,
Honorary Curator of Gems and Precious Stones, American Museum
of Natural History, and Special Agent for the United States
Geological Survey,

and
CHARLES BASKERVILLE, Ph.D., F.C.S.,
Smith Professor of Chemistry and Director of the Laboratory,
University of North Carolina.

THE purpose of this paper is to recount the results of our investigations as to the conduct of the gems and gem-material of the Tiffany-Morgan collection under the influence of Röntgen rays, ultra-violet light, and emanations of radium preparations. At the same time, through the courtesy of the American Museum of Natural History, we were permitted to make a careful study of the action of ultra-violet light upon the materials in the handsome Morgan-Tiffany and Morgan-Bement collections. These collections undoubtedly are the most complete authenticated minerals and gems on exhibition in the United States. The fluorescence and phosphorescence resulting from the action of ultra-violet light upon about 13,000 verified minerals were carefully observed. In addition to the above, we had an opportunity to submit selected stones from about 15,000 British Guiana diamonds, and two particularly handsome diamonds (one being a tiffanyite), and several carbonadoes, to these influences, the products of the most modern scientific investigations. Our first mention of this investigation was given briefly in *CHEMICAL NEWS*, vol. lxxxviii., p. 263.

As there is no uniform meaning accepted for the terms "fluorescence" and "phosphorescence," in the outset we wish to emphasise our interpretation. Jackson would have them meaning the same. Perhaps they are due to the same phenomena; but in this paper by fluorescence we mean a luminosity, more usually evidenced by a play of colour, lasting only during the direct influence of the exciting agent. By phosphorescence we mean the emission or propagation of ethereal stresses, which affect the optical centres, producing light, white or coloured, which persists after the removal of the cause. Substance may therefore be both fluorescent and phosphorescent.

The radium preparations of the highest activity used in these investigations became the property of the American Museum of Natural History through the liberality of Mr. Edward D. Adams, a member of the Board of Administrators of the Museum and of the New York Academy of Sciences. His gift of the necessary funds was applied to the purchase

of one portion of radium bromide of 300,000 activity, and another of 1,800,000; uranium being taken as the standard at 1. The preparations were obtained from the Société Centrale des Produits Chimique at Paris. Unfortunately, although the order was authorised and material assured, it has been impossible to obtain the bromide of the highest strength in time for presentation at this meeting. The results here announced have to do with the radium of 300,000 and of 7000 activity (chloride), and 240 (chloride), and of 100 radium barium carbonate. The compounds of lower activity were purchased by the authors.

Thorium dioxide does not become luminous in contact with the radium preparations we have been able to obtain, although Elster and Geitel state that a thorium oxide screen shows scintillating fluorescence even after positive electrification, similar to the zinc blende.

Why certain rays either alone or through their influence upon the surrounding media present the order of magnitude of visible light waves, we shall not undertake to say. It is quite evident, however, that particular substances, like the diamond, willemite, kunzite, &c., possess the power of "stepping up or down," as it were, the ethereal stresses propagated by the radium, so that visible rays result, or the bombardment of electronic emanations produce such an effect. The luminosity cannot be attributed solely to the α -rays, or helium, as thorium oxide does not respond (at least visibly to the eye unaided by magnifying lenses), unless it so happens that the helium exists in one radioactive body in a different form from that in the other. Further, we have tested a number of helium-bearing minerals, and none responded to the strong radium bromide. It appears that the luminosity of such substances so variable in their construction as those mentioned above may be accounted for in a measure by the physical explanations adverted to; yet the striking fact that four zinc compounds of totally different composition, willemite (zinc orthosilicate), zinc sulphide, zinc oxide, and kunzite (which contains a fraction of a percent of zinc), all respond in the most pronounced manner to radium emanations, could indicate the presence of a new element, a "radium-foil," as it were, or some unusual combination of known chemical integers, which synchronise with the activities of this unique body. One is immediately reminded of the actinium Phipson announced in the eighties as being present in zinc white. (This is not to be confounded with Debierne's actinium, resembling titanium, announced in 1898).

Selected gems were mounted in paraffin blocks held in wooden frames, obtained by pouring the hydrocarbon, after melting in a water-bath, into especially constructed boxes about 18 x 27 c.m. and 1.5 c.m. deep. The wooden bottoms attached to the frames by screws were readily removed. Each "plate" was numbered by placing small

* Extracts from Paper presented before the New York Academy of Sciences, October 6, 1903.

wire nails on the cersine. Where gems of the same class varied in colour they were arranged according to the spectrum as far as practicable. Comparisons as to colour effects could thus be had, but of course no comparison of penetrative effects, as the stones were of variable thickness and were all photographed in place.

These plates admitted of a careful comparative examination of the gems when subjected to the bombardment of the Röntgen rays produced by a Queen's self-regulating Crookes tube with a twelve-inch spark coil. Many radiographs were also obtained with variable exposures, the iron markers adverted to, through their impenetrability, serving to identify the plates.

Perhaps no such complete collection has been studied in this manner, although Doelter in 1896 published a most interesting study of the conduct of some sixty-five minerals and other precious stones when subjected to the Röntgen rays. During the same year, J. B. Cochrane published a very practical paper on the testing of precious stones by the X-rays. Without giving details, it may be said that their observations were verified, and, in general, it was learned that the penetration of gem material by the X-rays is a matter of degree rather than kind, and sharper contrasts were obtained with certain precious stones when they were surrounded by metals, like gold or lead, than was had when they were radiographed alone. The observations of the late Professor Ogden Rood on the deflection of X-rays by crystal or cut faces were verified.

J. E. Burbank, in 1898, published a work on Mineral Phosphorescence produced by X-rays. Of all the substances tried, he found "in general minerals containing ores of the metals are non-phosphorescent," and that fluorite and calcite seemed most suitable for experimentation. J. Trowbridge states:—"By them (X-rays) an electrical charge is communicated to fluorescent and phosphorescent substances. The resulting electrical energy, in being dissipated (by heat), produces the phenomenon of light" (see below). Thomas A. Edison directed the Röntgen rays upon some eighteen hundred chemical compounds, artificial and natural, seeking fluorescent screens. Later (1900), Bary examined the conduct of a number of salts under the influence of Röntgen rays. "Those which become fluorescent belong, with the exception of uranium, to the families of the alkalis and alkaline earths. Similar results were obtained by exposure to the radiations from a radio-active metal supplied by Curie."

Robert Boyle, in 1663, appears to have been the first to have made a truly scientific examination of the phosphorescence of diamonds, although the alchemist, Albertus Magnus, in the thirteenth century, said he had seen a diamond which glowed when it was put in water. Bernoulli remarked that when a diamond is rubbed on gold it becomes luminous "like a burning coal excited by the bellows," as Draper put it. "A light, too, that cannot be extinguished by water, and yet so ethereal and pure that it can set nothing on fire," attracts the scientific imagination as much to-day as it did then.

Two hypotheses were offered in the eighteenth century in explanation of phosphorescence:—

1. Lemery, in 1709, maintained that phosphorescent bodies act like sponges to light, absorbing it and retaining it by so feeble a power that very trivial causes suffice for its extinction.

2. Du Fay, in 1735, upheld that it resulted from actual combustion taking place in the sulphureous parts of the glowing body. He first noted the substance requires previous exposure to light; it glows in the dark with decreasing luminosity. Du Fay also observed the effect of interposing coloured glass between the phosphorescent body and the light.

In 1859, J. H. Gladstone, exhibited diamonds strongly fluorescent in the sunshine. Silvanus Thompson used one of these diamonds in 1896 in a lecture on luminescence at the Royal Institution.

We are wanting a complete history of fluorescence or phosphorescence, nor explanations of these fascinating

properties; but hints are given below which may serve to assist their elucidation.

M. Mascart and Chaumet examined a number of gems under the influence of violet light. One of us (Kunz), in 1889, with Mascart, and with Hallock in 1894, submitted bluish-white, opalescent diamonds (from Bagagem Mines, Brazil,—tiffanyite) to electric light passing through glass of different colours.

Although, as will be mentioned, such compounds as alumina, alkaline earth sulphates, and certain rare earth oxides have been examined in vacuum tubes under the influence of electric sparks, we are not aware of any very extended examination of mineral or chemical substances when subjected to ultra-violet light produced by sparking. E. Becquerel in his "La Lumière ses Causes et ses Effets" states that "the electric spark acts only by its light, but its action is more energetic than that of the sunlight by reason of its great intensity and the proximity of the source." Wiedemann and G. C. Schmidt, in an article on luminescence, reached the conclusion that the violet light alone of the electrical discharge does not cause phosphorescence, but is "due to peculiar discharge rays analogous to cathode rays." M. W. Hoffmann confirmed the above. J. Trowbridge reported "the action of the X-rays on this mineral (fluorite) was exactly similar to that of electrification," and concluded, "by them (X-rays) an electrical charge is communicated to fluorescent and phosphorescent substances."

While there may be no question as to the statements above for the particular materials examined—and they are doubtless true for many other substances—yet below may be found observations which do not admit of the sweeping conclusion that all fluorescent and phosphorescent phenomena observed in minerals subjected to rays coming from the sparking of high voltage currents with iron terminals are due to electrification.

The ultra-violet light was produced by a triple spark through quadruple iron terminals (we may so designate them) with a high voltage current. The direct current was taken from a 110 volt circuit passed through a Ruhmkorff coil with a 12-inch spark and stepped up by two Leyden jars in series. The spark was provided with a quartz window surrounded by vulcanite and otherwise insulated to permit comfortable handling. As the number of observations to be made was very great, it was impracticable to remove each individual specimen from the exhibition cases and storage cupboards to the dark room, although this was done in many experiments. Flexible cables 200 feet long were joined to the apparatus. This was placed upon rollers, and could be moved easily to the various aisles between the cases. The Piffard lamp was joined up with the apparatus by insulated wires, further protected by rubber tubing 36 feet long. About 13,000 minerals were thus examined by night.

A large mass of original material has been gathered, of which only a few general observations and tentative conclusions are presented.

The two most responsive minerals to all three forms of activity were found to be willemite and certain diamonds.

1. It was found, as doubtless observed by others, that willemite from Franklin, N.J., is both fluorescent and phosphorescent with the Röntgen rays, ultra-violet rays and when exposed to radium emanations. These properties were retained, although in some instances the specimens were considerably altered by decomposition. Foreign specimens of the same species were not affected at all. The willemite retained its luminescence for more than twenty-four hours after it had been exposed to radium; the latter not being then within 100 feet of it.

2. The calcite from Franklin, N.J., showed a distinct red glow with the ultra-violet rays. This mineral, as well as the willemite, showed very marked peculiarities of colour; the willemite green and yellow-green, the calcite a red glow. These effects were so characteristic that it required but a moment to identify the specimens encountered

RADIO-ACTIVE MINERALS.

Mdme. Curie's Table of Amperes.
Intensity 1.

Kunz-Baskerville observations on phosphorescence of minerals with

		Ultra-violet light	Röntgen rays
Uranium	2.3		
Pitchblende from Johanngeorgenstadt	8.5	-	-
Pitchblende from Joachimsthal	7.0	-	-
Pitchblende from Příbram	6.5	-	-
Pitchblende from Cornwallis	1.6	-	-
Cleveite	1.4	-	-
Autunite	4.7	+	+
Sipylite	-		
	0.1	Amherst County, Virginia	-
	0.3	Barkevik, Norway	-
Various thorites	0.7	(Auerlite), Green River, North Carolina	-
	1.3		
	1.4		
Orangite	2.0	Arendal, Norway	-
Monazite	0.5	Cheyenne Cañon, Colorado	-
Xenotime	0.03	Alexander County, North Carolina	-
Æschynite	0.7	Hitteroe, Norway	-
Fergusonite (two samples)	0.4	Llano County, Texas	-
	0.1	Ytterby, Sweden	-
Samarskite	1.1	Berthier County, Quebec	-
Niobite (two samples)	0.1		
	0.3		
Tantalite	0.02		
Carnotite	6.2		
Columbite	-	Portland, Connecticut	-
	-	Arendal, Norway	-
	-	Zlatoust, Ural	-
Monazite	-	171st Street and Washington Avenue, New York City	-
	-	Amelia Court House, Virginia	-
	-	Alexander County, North Carolina	-
	-	Rio, Brazil	-
Monazite sand	-	Tvedestrand, Norway	-
Monazite	-	Near Marietta, South Carolina	-
Polycrase	-	Mitchell County, North Carolina	-
Euxenite	-		

Column 1 is Mdme. Curie's list of rare minerals; 2 is Kunz and Baskerville's ultra-violet ray; 3, Röntgen rays. With one exception, neither of the latter show any action.

in various parts of the collection, without seeing the label, as being from Franklin, N.J.

3. The gangue of all minerals from Pajsberg and Langban, Sweden, also showed this peculiar red glow; the limestone strikingly like the calcite from Franklin, N.J.

4. All the minerals from Mono Lake, California, the colemanite, hanksite, glauberite, iddingsite with ultra-violet rays. The briefest exposure causes them to glow and to retain this luminescence for a considerable time; but none of these minerals either phosphoresced or fluoresced with radium; those tested with magnesium light phosphoresced.

5. Hydro-zincite, from Algiers, showed a remarkable fluorescence, bluish in colour, different from anything in the collection.

6. Autunite and another uranium mineral, from Mitchell County, N.C., fluoresced wonderfully, while foreign specimens of the same species did not. Autunite appears to have two minerals present with it, one an orange and the other a lemon-yellow; one pulverulent and the other in slight tabular crystals. The striking fluorescence obtained with ultra-violet rays was not produced when glass, which is opaque in these rays, was interposed.

The yellow mineral labelled greenockite, from Franklin, N.J., fluoresced in an identical manner, leading one to infer that this is itself a uranium mineral, or else contains the same substance that causes the autunites to fluoresce.

A comparative table is appended. It is self explanatory, and serves to illustrate the conclusions apparently inevitable, namely, the presence of something not previously recognised.

7. Hyalite (botryoidal), on a trachytic rock, from San

Luis Potosi, Mexico, as colourless as the purest water, fluoresced most intensely with a rich British green colour, but these specimens did not phosphoresce. This green fluorescence could be observed when the source of the ultra-violet was five or six feet away. It did not persist on the removal of the source, but flashed in when the rays played upon it. The sparkler held near, but without the rays playing upon the specimens, gave no fluorescent effects. Therefore no other conclusion is tenable than that it is the ultra-violet rays that produce this change. The same remark may be made for many of the experiments carried on with the sparkler as the source of the ultra-violet light in the examination of these mineral substances. On the other hand, this hyalite neither fluoresced nor phosphoresced when exposed to the magnesium light, Röntgen rays, or radium. In this respect it behaves like the minerals from Mono Lake. No hyalite from other localities responded to any of these activities.

8. By the action of ultra-violet light rays a number of fluorites both phosphoresced and fluoresced; some phosphoresced, and did not fluoresce; some fluoresced, and did not phosphoresce; and some did neither. Further, their colour had apparently no influence in determining this result. It cannot be the fluorine or alkaline earth present that account for this variation. It is more probably the presence of rare earths, such as yttrium and ytterbium. (See *CHEMICAL NEWS*, vol. lxxxviii., p. 263).

9. Chlorophane has long been known as a mineral very easily rendered luminous by heat. By some authorities it was stated, a century ago, that it was almost always luminous. This variety of fluorspar is found with other fluorspars—sometimes as a vein of purple between veins of

green fluorspar. It proved very responsive to the ultra-violet rays. A variety from Amelia Court House, Virginia, became suddenly luminous from the heat of the hand. This luminosity was lost upon further heating (about red heat), but the phosphorescent properties were restored in a measure by exposure to the Röntgen rays. Trowbridge has observed this with other fluorites (see above). The exquisite coloured fluorescent properties were not regenerated, however. Chlorophane is pyroelectric by attrition, and this peculiarity distinguished it from the ordinary fluorites.

10. It was noted that gypsum from Sicily, when submitted to ultra-violet light, was from two to five times as responsive as specimens from Bavaria and other localities.

11. It was found that those topazes which had lost the sherry colour—the tint so fleeting that some of the museums have been led to protect them from the light—showed no distinct phosphorescence with ultra-violet rays, while the unfaded crystals of that colour responded, but no others.

12. Wenerite from New York phosphoresced, while specimens from foreign sources did not. Many apophyllites and calamines gave no response whatever.

13. Pectolite proved an exceptionally interesting mineral. Every specimen that was exposed to the ultra-violet rays showed an active response; even some that were almost entirely altered to steatite. This is especially striking as some of the specimens from New Jersey were loose delicate aggregates of needle-like crystals. Some were made up of crystals with a texture like felt, others of coarse crystals, and, lastly, the pectolite without any crystalline structure, homogeneous, and one time mistaken for jade, from Tehama County, California.

14. Wollastonite, whether from northern New York, or associated with the rosolite garnet from Mexico, phosphoresced markedly and with some duration, with ultra-violet rays, and responded strongly to radium (300,000).

15. Kunzite, the new variety of spodumene from Pala, California, when exposed to the action of radium of 300,000 activity for a few minutes, became wonderfully phosphorescent, the glow continuing persistently after the removal of the source of excitation. Six hundred grms. of kunzite crystals were excited with 125 m.grms. of radium bromide. Sir William Crookes, in a personal letter, having repeated the experiment, remarks:—"I think this lilac variety of spodumene runs the diamond very close, if it does not surpass it sometimes." Ultra-violet rays caused kunzite to phosphoresce for more than a minute. This remark applies also to the faded or colourless kind. All forms of kunzite became strongly phosphorescent with the Röntgen rays. So pronounced is this that a large crystal excited for five minutes afterwards affected the film of a sensitive photographic plate. And a thirty second exposure caused those gems to glow first golden pink, then white for ten minutes, twenty times the duration of exposure to the X-ray, the glow penetrating two thicknesses of white paper. It is also pyroelectric, assuming a static charge, similar to topaz, when rubbed with a woollen cloth. It does not phosphoresce when heated.

16. The action of the quartz group was interesting. As a rule, quartz proper neither phosphoresced nor fluoresced with ultra-violet rays, allowing them to traverse it without any effect. Hence, the very few exceptions noted were doubtless due to the inclusion of intermixture of other substances. This was apparent in one or two cases of quartz pseudomorphs after barite and fluorite, which phosphoresced evidently from the presence of some remainder of that mineral.

Chalcedonic quartz was also very unresponsive; one example only, from Uruguay, S.A., showing a bluish milky phosphorescence, and a specimen of agate, in which one layer responded between others that did not.

Opal, on the other hand, is frequently phosphorescent, very rarely fluorescent, and sometimes without any action. The variety quincite phosphoresced intensely, as did also

specimens apparently pseudomorphous after gaylussite, which exhibited strong and long continued phosphorescence.

17. Among carbonates, calcite, witherite, strontianite, and barytocalcite, all phosphoresce with ultra-violet light; while arragonite, with occasional exceptions, is very marked in its action, far surpassing calcite. On the other hand, cerussite does not phosphoresce, save in a single specimen from Phoenixville, Pa.

There is here seen again a peculiar phenomenon in minerals from Langban locality, and the suggestion is evident of the existence there, and at points where similar exceptional results appear, as in Mono Lake, of the presence of some rare element (perhaps new) widely diffused in very minute quantities.

A similar indication is given by the behaviour of the glauberite; those from Borax Lake, California, phosphoresce, as do those from Laramie, and from Spain; while Chilean specimens do not.

18. It is notable that tourmaline, which is so markedly pyroelectric, gives no response to ultra-violet light; nor does beryl, save in three specimens from Haddam Neck, Conn.

19. American sapphires of various kinds, spinel, chrysoberyl, and almost all jades, declined to show any effects from ultra-violet rays. Many of the gem minerals, except diamond, opal, and kunzite, are little acted upon.

20. Only two of the rare earth oxides artificially prepared, responded at all to the action of ultra-violet rays, namely, zirconium and thorium dioxides, which phosphoresced strongly. The thorium dioxide remained luminous in the dark for a greater length of time. The zirconium dioxide showed no radio-activity when tested by the electrical and photographic methods. It is strange that two earths forming dioxide are the only ones to exhibit this property. The following oxides were examined:—Yttrium, ytterbium, erbium, gadolinium, samarium, lanthanum, cerium, neodymium, praseodymium, thorium, zirconium, titanium, uranium, and variable mixtures of the same. They will be investigated further by one of us (Baskerville).

In view of the fact that these two earths give this characteristic response to ultra-violet light, it became immediately of interest to learn the effect of the light upon minerals carrying those substances in different proportions. The following selected minerals were again subjected to the action of ultra-violet light without a single one of them giving either fluorescence or phosphorescence:—

Samarskite—Berthier County, Quebec.

Thorite (Orangeite)—Arendal, Norway.

" —Barkevik, Norway.

" (Auerlite)—Green River, North Carolina.

Sipylite—Amherst County, Virginia.

Columbite—Portland, Connecticut.

Monazite—Arendal, Norway.

" Zlatoust, Ural.

" 171st Street and Washington Avenue, New York.

" Amelia Court House, Virginia.

" Alexander County, North Carolina.

Monazite Sand—Rio, Brazil.

Monazite—Tvedestrand, Norway.

Xenotime—Cheyenne Cañon, Colorado.

" Alexander County, North Carolina.

" Hitteroe, Norway.

Euxenite (in *Samarskite*)—Mitchell County, North Carolina.

Æschynite—Hitteroe, Norway.

Polycrase—Near Marietta, South Carolina.

Fergusonite—Llano County, Texas.

" Ytterby, Sweden.

Tentative Conclusions.

1. It seems as though in willemite, hydrozincite, and in the artificial phosphorescent zinc sulphide, zinc oxide, and kunzite, there is present, with the zinc, some element probably not yet determined, that possesses peculiar prop-

perties; or one that in combination with a zinc mineral gives the high luminosity by the application of radium, with the ultra-violet rays, or the Röntgen rays, or other radio-active bodies; an element possibly accompanying zinc and possessing an affinity for it, as polonium has for bismuth, perhaps Phipson's actinium, adverted to.

2. It seems likely also that there exists in fluor spar either yttrium or ytterbium or some other related rare earth, or perhaps several of them, from the variable action of this mineral with the various kinds of rays.

3. When we consider the diverse composition of the numerous minerals coming from Borax Lake, and that it consists of the evaporated remains of an inland sea, there seems to be present some element which is very highly active, but is not responsive to radium, and which appears in every single mineral found here. This is evidently a substance not necessarily radio-active itself, but one that may possess the same or allied properties with the substance found with the zinc-minerals.

4. The substance present in calcite, from Franklin, N.J., and from Langban and Pajsberg, Sweden, is probably yet another body, as it does not respond to radium; although the willemite found with it at Franklin becomes luminous at the approach of radium or ultra-violet light, as if they were fairy wand.

5. There probably exists in autinite, and another yellow-brown uranium mineral from Texas, a fluorescent substance which differs from anything we have noted in the study of the minerals of the collection.

6. In the hyalite from San Luis Potosi, a volcanic mineral, there is present something that responds with a beauty of colour that strikingly reminds one of nitrate of uranium; this is probably a physical change, yet may prove to be still another substance.

7. The most responsive of all, however, were the diamonds containing that peculiar substance that gives them what is known as the blue-white colour—fluorescent like anthracene, and holding the luminosity for a long time—to which one of us (K.) gave the name of Tiffanyite in 1895.

In the examination of more than 15,000 diamonds from British Guiana and elsewhere, 44 were selected. After an exposure of 60 seconds to ultra-violet rays, these 44 diamonds phosphoresced brilliantly and continued to glow for a long time after exposure. The luminosity was so great that it penetrated one thickness of white velvet and from nine to twelve thicknesses of tissue and blue linen paper. But they did not exhibit their light through black velvet, nor apparently were they affected by the ultra-violet rays when surrounded by black velvet. These diamonds when glowing brilliantly showed absolutely no action upon the barium platino-cyanide screen, nor upon screens of phosphorescent zinc sulphide or calcium sulphide.

The most remarkable specimen was a diamond of 151 carats. (This was exhibited). This stone possesses the power of absorbing sunlight and emitting it in the dark. An arc lamp will cause it to store up energy and to give it out as light in the dark. Even a small hand-lamp of one candle power has caused this diamond to phosphoresce. It responds to polonium, to the Röntgen rays, and to the ultra-violet rays; to the rays that pass through a violet glass, and to radium, even in a more marked degree than willemite.

The print shown was made from a negative obtained by exposing a sensitive photographic plate to the 15 carat blue-white and a 15 carat transparent black stone, thin white paper intervening, after they had been exposed to ultra-violet light for one minute. The print is the result; except that the print of the black stone has been coloured to show the reddish phosphorescence given out by it.

After another exposure of one minute, to our surprise the black stone glowed red for fifteen minutes, almost surpassing the white phosphorescence of the blue-white stone. At the end of fifteen minutes the red glow subsided, while

the white stone phosphoresced five minutes longer; the light being held twenty minutes after exposure.

As stated above, from the work of Wiedemann and Schmidt, Hoffmann and Trowbridge, it appears that the phosphorescent and fluorescent effects observed by the action of ultra-violet light produced by sparking with such metals as iron, is not due to this cause at all, but may be accounted for by the accumulation of an electric charge. The diamonds were "grounded" by placing directly upon the iron radiator in the room and similar observations made, as when the precious stones were insulated.

It is interesting here to note that Marckwald reported the property of phosphorescence with polonium as belonging only to Brazilian diamonds. Rosenheim found that the rays from radio-active polonium possess the property of inducing fluorescence in a number of diamonds from different localities. The rays emitted by the diamonds under these conditions affect the retina and photographic plate. "This actinic activity of the diamond," he says, "like its visible fluorescence, is entirely dependent on the presence of the polonium, not persisting after the removal of the latter. Even after long exposure to polonium rays no induced radio-activity could be detected."

Almost all diamonds of various weights and from many localities and different colours, fluoresce and phosphoresce more or less with radium, except the black or carbonado. The degree to which these phenomena are observed is no criterion of the grade of the gem, however, as stones with flaws often fluoresce with even greater brilliancy than the pure jewels.

8. It is quite evident through our study of the collection that one or the other of these forms of luminosity and activity may have a value to detect elements or compounds that have escaped notice or are present in the minerals as impurities. These forms of investigation may also prove of value in chemical analyses. There should be a use for this line of research also in petrological determinations, as the slightest phosphorescence or fluorescence would aid in determining and locating a mineral, no matter how minute in quantity. This we have done in several instances.

The original ultra-violet lamp was that of Gorl, of Munich, altered by the English into the St. Bartholomew lamp, and again improved and made practicable in the United States under the name of the Piffard lamp, after Dr. H. G. Piffard, of New York, who has used it with much success in medical practice. It is an instrument of great utility, and, in the convenient form with which we worked, cannot fail to prove a valuable mineralogical and chemical as well as medical adjunct. The lamp will be useful in many instances for mineralogical determination, at times to detect impurities which have escaped analysts and others.

9. In all observations on the effect of radium, ultra-violet light, and the X-rays to determine whether an object becomes fluorescent or phosphorescent under the influence of either, it is essential that the eyes become thoroughly accustomed to the change of conditions when one is in a dark room.

This usually requires from ten to twenty minutes, and in some cases half-an-hour. Attention to this has been called by preceding observers. Whether it be due to the accumulation of the visual purple, which von Kries states is a substance that supplies the retinal basis of vision at low luminosities, and whose accumulation is accountable for the great increase in sensitiveness of the dark adapted eye, or to the ordinary physical changes in the optical lenses, or both in part, we do not undertake to decide. But it was learned that it was advisable just before the source of excitation was removed from the material examined that the eyes be closed and opened again after the removal. Else, as was noted, the residual flash that remained may be mistaken for phosphorescence. In most of the experiments carried out three observers watched each test. When there was the least disagreement, the tests were

repeated a sufficient number of times until a unanimous agreement was arrived at,

10. The Röntgen rays have been used with great success to locate fractures, mis-growths, deformities, and abscesses in the bony processes; but as far as we are aware, little success has attended efforts to locate ruptures, growths, or peculiarities of the veins, intestines, &c., by this means. There seems a possibility, however, that if a highly fluorescent or phosphorescent substance could be injected into the veins, the stomach, or the intestines, it would be feasible to locate lesions, growths, and other peculiarities of these organs; possibly also to locate accretions and kidney or bladder concretions, especially calcareous, as well as, possibly, peculiarities in the structure of the heart and other organs. This it might be practicable to do by means of inert but phosphorescing materials in solution given in the food, or injected into the stomach or intestines when they are quite empty. It might be that a nearer location could be effected in the organs desired to be examined if impalpable powders be given with the food. If it were possible to inject such a substance into the blood, the entire vein structure of the body might be rendered visible as well as the bony part. It seems not unlikely that such an active agent as radium, or ultra-violet light, may yet be found a great accessory in diagnosis and autopsies, as they have given promise of marvellous curative values in certain diseases. After presenting this paper we were informed that Dr. Morton and Mr. W. J. Hammer have investigations along these lines now in progress. The latter has prepared a highly interesting lecture on radium.

11. The final part of the work planned was an investigation of the influence of cathode rays upon gems and the gem material of these collections. The method utilised in the classical investigations of Becquerel, Crookes, and de Boisbaudran on the fluorescence and phosphorescence of a number of substances, especially alumina and the rare earths, *in vacuo*, and spectroscopic examination of the light emitted therefrom, offer possibly an answer to questions as to the nature of such substances as give tiffanite its unique properties, for example. Small amounts may be used; the destruction of such valuable gems in chemical analysis being out of the question. The time at our disposal having been utilised in securing the observations briefly outlined above, we were forced to discontinue the research for a time to work up a great quantity of experiments made of which these are only a few, although a number of Crookes tubes have been charged with material and exhausted. We hope to complete the phase of the undertaking, but confess, from what has been indicated above, that things have been seen that shine like a "pillar of fire by night," and beckon us on.

12. From the summarised observations on minerals recited above, it appears that there are evidently two properties recognisable—radio-activity and a property that responds to this activity. It is hence seen that we have two classes of bodies—radio-active and those that are affected by radio-activity; and that these groups may be again divided into several minor divisions:—

1. Those that respond to the radio-active bodies.
2. Those that do not respond.
3. Those that respond to ultra-violet rays.
4. Those that respond to Röntgen rays.
5. And then again, some will not respond to either one, two, or all of the three forms.

We seem to find here an analogy to certain well-known facts in electricity and magnetism; some bodies that are active, and others that are acted upon in several different forms, which are evidently closely related, and yet are distinct in their modes of action. We are privileged, therefore, to offer for mineral substances a—

Tentative Classification.

Those minerals:—

1. Not responding to radium, ultra-violet, or Röntgen rays.
2. Responding to radium only.

3. Responding to ultra-violet rays.
4. Responding to Röntgen rays.
5. Responding to radium and ultra-violet rays (not to Röntgen rays).
6. Responding to radium and Röntgen rays (not to ultra-violet rays).
7. Responding to ultra-violet and Röntgen rays (not to radium).
8. Responding to radium, ultra-violet rays, and Röntgen rays.

As for mineralogical determination, no large apparatus is necessary as is used in medicine or physiological investigations. In fact very simple apparatus is sufficient. Therefore we are devising a series of appliances so that the entire apparatus may probably be purchased for much less than one hundred dollars.

We are also preparing a list of minerals, selecting those most readily obtainable, to illustrate these phases of activity or inactivity with the three useful accessories. For a small expenditure any school or college can obtain them for comparative study.

As the electric furnace has given us *carborundum*, artificial graphite, and a series of absolutely new carbides, because with it we have attained temperatures of a height unknown before its introduction—as the production of low temperatures has resulted in the liquefaction of all known gases and assisted in the discovery of new ones—so perhaps the application of these forms of energy may give us the means of identifying substances that all our earlier methods of observation have escaped; and it may be that we shall have a new series of elements. We are clearly on the threshold of a new field of scientific facts, and perhaps generalisation and laws, which may yield results in the twentieth century as interesting and remarkable as the electrical discoveries were in the nineteenth. Indeed, some have already discarded atomic chemistry and assumed ionic chemistry, while pioneers like Crookes, J. J. Thomson, and Lodge vouchsafe "protyle," "corpuscles," and "electrons," with more or less experimental verification, although they do not quite reach Ostwald's metaphysical view.

Here we have to mention the aid given us in having access to the collections, the construction of a special dark room, every facility of the Museum's workshops, the encouragement and advice given by the Museum's able director, Dr. H. C. Bumpus, and to the attention and assistance of Dr. L. P. Gratacap, and Mr. L. P. Seymour, and Mr. Smith, of the Mineralogical Department, and Mr. Dahlgren, the Museum photographer.

POTABLE WATERS IN SOUTH-WEST LANCASHIRE.*

ON THE NATURE AND QUALITY OF SOME POTABLE WATERS IN SOUTH-WEST LANCASHIRE.

By Professor J. CAMPBELL BROWN, D.Sc.

THESE waters may be classified under three heads:—

- I. Surface waters.
- II. Deep-well or bore waters.
- III. Shallow-well or spring waters.

I. The earliest of the first class is the Rivington supply, introduced into Liverpool in 1857. Although this water has been in daily use for forty-six years, and has received analysis for sanitary purposes frequently from 1850 down to the present year, no complete analysis of the mineral constituents has been made by anyone, so far as I have been able to ascertain. I therefore made a full analysis a short time ago for the purposes of this paper. It is interesting

* A Paper read before the British Association, Southport Meeting, 1903.

RESULTS OF ANALYSIS EXPRESSED IN PARTS PER 100,000.

	1	2	6	7	8	9	10	11	12	13
	Grimsby	Spide Mill	Dhworth	Tilled and	Quarry	Sandston- colliery	Quarry	Netherley Well		
Total solids	—	1812	1862	2874	4478	4078	1850	1882	1897	1961
Organic carbon	—	—	—	—	—	0.064	—	16.6	16.6	15.2
Organic nitrogen	—	—	—	—	—	0.023	—	0.049	0.049	—
Oxygen consumed in fifteen minutes	—	0.084	—	—	—	0.060	—	0.021	0.021	0.001
Oxygen consumed in three hours	—	0.460	—	—	—	0.012	—	0.012	0.012	0.002
Ammonia	0.011	0.002	0.011	0.002	0.000	0.002	0.004	0.000	0.002	0.003
Ammonia by distillation with alkali	0.021	0.012	0.012	0.002	0.010	0.000	0.003	0.002	0.000	0.000
Nitrogen as nitrates	0.021	0.021	0.000	0.000	0.024	0.000	0.035	0.175	0.241	0.3
Combined chlorine	1.1	1.1	1.3	2.2	2.3	1.8	1.8	2.3	2.2	2.23
Temporary hardness	—	—	—	—	—	27.5°	—	24.3°	0.72°	3.27°
Permanent hardness	—	—	—	—	—	7.5°	—	7.57°	6.71°	6.73°
Total hardness	—	—	—	—	—	35°	10°	10°	7.43°	10°
Neutral: contain iron, but no iron organisms.										
Alkaline: contain iron, but no iron organisms.										
Alkaline: contain iron, but no iron organisms.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any kind in this water.										
No organisms of any										

to compare the figures with those of an analysis of the Vyrnwy supply made for the Corporation of Liverpool in 1898.

Analyses Expressed in Parts per 100,000.

	1. Rivington water. Clear, but not filtered.	2. Vyrnwy water. Strained, but not filtered.
	1903.	1898.
Total solids in solution..	10.16	3.98
Loss on ignition	2.74	1.05
Alkalis	1.06	0.518
Magnesia	0.461	0.127
Lime	1.735	0.706
Oxide of iron	0.016	0.099
Oxide of manganese ..	0.017	0.059
Chlorine	1.500	0.6
SO ₃	2.144	0.6
Silica	0.463	0.214
Total mineral matter ..	7.417	2.923
Combined CO ₂	none	none
Organic carbon	0.343	0.498
Organic carbon after filtra- tion	0.323	0.331
Organic nitrogen	0.064	0.064
Organic nitrogen after filtration	0.052	0.042
Nitrogen as nitrates ..	trace	0.109
Ammonia	0.003	0.006
Ammonia from distilla- tion with alkaline per- manganate	0.009	0.017
Oxygen required to oxidise in fifteen minutes ..	0.048	0.048
Oxygen required to oxidise in three hours	0.084	0.296
Acidity due to organic matter equivalent to CaO	0.19	0.2
Dissolved gases per litre:—		
Oxygen	—	5.45 c.c.
Nitrogen	—	11.53 "
CO ₂	—	none

The most important practical difference is not very evident on the face of the analytical figures, and I may as well point it out. It is the much smaller quantity of organic compounds of iron in the Rivington water. The difference in the iron is as 0.016 in Rivington to 0.099 in Vyrnwy.

There is no means of exactly determining quantities of organic matter itself. Perhaps the best figure showing the difference to which I allude is that for oxygen consumed in three hours—namely, the ratio of 0.084 in Rivington to 0.296 in Vyrnwy.

The practical difficulties due to this difference are:—

1. Filtration and decolorisation.

2. Action on lead.

3. Obstruction of the pipes by deposits and growths.

The Rivington water is slightly coloured and contains a small quantity of organic compounds of iron, to which colour is generally due. Although the two waters are so much alike, there is none of that development of iron organisms in Rivington water which is so common in Welsh waters like that of the Vyrnwy. It is excellent water for domestic use, and is likely to remain so, now that Liverpool has the power to repress the pollution of the watershed by dwelling-houses, inns, and farms.

Good examples of Lancashire catchment waters are those supplying Preston, Nos. 3 to 6. Occasionally agricultural land yields good water, as in No. 7. But water from agricultural land generally yields water too impure to be fit for domestic use. Intermediate between surface water and well water are waters collected in quarries. Nos. 8, 9, and 10 furnish examples of these.

The head waters of most of the Lancashire rivers are also of good quality; but by the time that they reach south-

west Lancashire they have received so much pollution, both from human dwellings and manufactories, that it is impossible to use them, and they need not be further mentioned here.

II. *Deep-Bore Water.*—The City of Liverpool was, until recently, supplied to a great extent from deep wells and bores in the sandstone. The rock is becoming gradually saturated with the partly oxidised waste water of our sewers and streets, and the wells are, one after another, falling into disuse, only three being still in use for public supply. In smaller places deep wells are still the best kind of supply.

As typical examples of good deep-bore water from the Keuper sandstone of Lancashire, two wells supplying Widnes may be mentioned—Analyses 11 to 16.

It is interesting to compare the composition of the same bore at different depths. Nos. 17 to 19 show the quality of the water at different depths of a deep bore at Newton. This is typical of many bores in Lancashire and Cheshire, which have been examined as the bore was deepened.

Nos. 20, 21, and 22 are deep wells in the St. Helens district.

No. 23 is from a deep well in the Ormskirk district, where much lime and magnesia are found in all the underground waters.

III. *Shallow Wells.*—Shallow wells—that is, wells under 32 ft. in depth—which are still the chief source of supply in country places, vary greatly in composition, and are usually unfit for domestic use. A well must not, however, be assumed to be bad because it is shallow. Those which yield good potable water have generally but small quantities of solids in solution; they are soft, almost free from nitrates, have no nitrites, the figures for ammonia are high, and they consume much oxygen. They are alkaline as a rule, except towards the Yorkshire side, and contain numerous and varied organisms—vegetable, such as diatoms, desmids, confervæ, and bacteria; and animal, such as cypods, paramécia, and many others.

Exceptions occur in which the total solids are very high; for example, in No. 25 the total solids in solution amounted to 108 parts per 100,000; in No. 26 to 112.5—this was ferruginous, but contained no living organisms; and in No. 27, 175.6. This last was the only potable water available, and therefore it had to be used, although the dissolved salts were so excessive.

IV. Although the iron organisms which have given much trouble in some Welsh waters have created no similar difficulties in Lancashire, this is not because they are altogether absent, but because they do not flourish and multiply.

Iron Organisms in Lancashire Waters.

Attention was first directed to the occurrence of deposits formed by iron organisms in potable waters in Lancashire in the winter of 1890-91, when decomposed vegetable masses and strings of bacteria—in their earlier forms, nearly colourless, and in their older state strongly coloured by ferric oxide—were observed in water coming from the deep bore of Bootle well belonging to the Corporation of Liverpool.

These ferruginous strings were reported at the time to be "tangled masses, enclosing in their meshes particles of sand and filaments."

These red masses came up with the water of the 1300 ft. deep bore.

They were deposited and grew on the stones lying in the well and headings. They were liable to be drawn up by the pumps and pass into the water supply. They had no effect on health, but were unsightly, and they therefore required investigation and repression.

Under the microscope they resembled the iron organisms known at that time by the name of *Crenothrix Kuhniana*, which had caused a great deal of trouble in the water reservoirs and channels of the waterworks of Rotterdam and Berlin by increasing to such an extent as to interfere with

the flow of water, and which have since been found in other Continental water supplies.

They were traced as far down in the 1300 ft. bore as 700 ft. At that point they were being carried up with the water from a great depth, and were in a living state, capable of being kept alive in the laboratory.

The water of this bore, like that of the Bootle well generally, was well aerated.

They were not formed in the 700 ft. bore adjoining, nor in any of the sixteen other bores which had less depth, although they grew freely on stones in the mixed water from all the bores.

The occurrence of these organisms in the well water was checked by plugging the deep bore. After this they disappeared from the well and did not find their way into the other bores. The large quantity of organic matter in the deep-bore water containing the organisms is noticeable, compared with the quantity after the deep bore was plugged, and has probably afforded food for the iron organisms.

I have shown elsewhere that the multiplication of these organisms is dependent on the presence in the water of an organic compound of iron, having an acid reaction.

The next occasion on which iron organisms were observed was in 1892, in water from agricultural land, which gave a slight deposit of iron oxides, with diatoms, and a few iron organisms. A well near Wigan, and another water near Garstang, in 1894, contained them, although they did not develop to any extent. Neither sample was acid, but contained a little iron and organic matter.

Composition of Bootle Well Water in 1890-94.

	1890-91.	After plugging deep bore, February, 1891.	1894.
Total solids	40	42·08	42
Ammonia	0·003	0·003	0·000
Ammonia yielded by alkaline permanganate ..	0·004	0·006	0·000
Organic carbon	0·152	0·065	0·052
Organic nitrogen	0·034	0·011	0·022
N as nitrates	0·401	0·459	0·459
Chlorine	4·2	4·1	4·1
Hardness	25°	26°	26½°

No iron; alkaline reaction; no organisms.

The only example of water containing bicarbonate of lime which I have met with containing any iron organisms was one in 1895. It was from a shallow well with an iron pump, and they did not develop to any extent.

Analysis Yielded

Total solids.. .. .	74·08
Ammonia	0·004
Ammonia by permanganate ..	0·008
Nitric nitrogen	0·371
Combined chlorine	6

No iron in solution, but a slight deposit derived from the pump; there was a white scum formed by evaporation of the carbonic acid; also decayed vegetable matter, and a few iron organisms (*Cladotrix*).

Two examples occurred in 1896 from a spring well after the water, which was neutral, had been conveyed in iron pipes. The water contained organic matter, and the organisms did not develop much in either case.

In 1899 they were found in a tarn in the Lake District which contained 9 parts of dissolved salts, including 0·2 part of dissolved oxide of iron per 100,000. These waters contained also organic matter and were acid, and developed an organism which was at that time called *Cladotrix dichotoma*.

THE SOLUBILITY OF HYDRATED SULPHATE OF LIME IN SOLUTIONS OF SEA-SALT.

By ALEX. D'ANSELME.

SATURATED solutions of chloride of sodium (natural brine), which serve as the raw material in the manufacture of soda-ammonia, are obtained by dissolving the solid sea-salt obtained from salt marshes, in fresh water free from salts of magnesium.

These solutions always contain a considerable proportion of sulphate of lime, which is always greater than the proportion of this salt soluble in pure water.

Analyses made regularly for several years, dealing with hundreds of thousands of tons of the dissolved salts, have never given less than 2·5 grms. of SO_4Ca per litre of brine.

This shows that commercial chloride of sodium always contains sulphate of calcium, which confirms the observations of M. Cloez in a recent paper (*Bull. Soc. Chim.*, Series 3, vol. xxix., p. 167). This impurity is of considerable inconvenience in the utilisation of these brines, as it is precipitated under the influence of currents of $\text{CO}_2 + \text{NH}_3$ gas.

The examination of these solutions, undertaken some months ago, has led me to determine the solubility of sulphate of calcium in solutions of chloride of sodium of different strengths, and at about the ordinary temperatures.

Chemically pure solutions of chloride of sodium, of which the concentration is in simple relation with the normal strength, are brought into contact with an excess of pure sulphate of calcium, and agitated in a continuous and regular manner. For this purpose the flasks are fixed on to a wheel revolved by a dynamo.

The whole is plunged into a thermostat, which assures a constant temperature during the whole of the experiment, at least within a degree.

Under these conditions, I made experiments on the time necessary to reach equilibrium, by taking samples of the liquid every hour from the same flask in the presence of a continual excess of SO_4Ca . Equilibrium was always reached in less than three hours agitation. Nevertheless, my definite final analyses were not made until after nine or ten hours of continuous agitation.

The lime, precipitated by CO_2Am_2 , was estimated first in the form of pure CaO , then in the form of sulphate, after having been taken up with sulphuric acid.

Two series of experiments were made, one at 14°, the other at 20°.

Results found.

NaCl, per litre.		Anhydrous SO_4Ca dissolved, per litre.	
Grms.	Molecule.	At 14°.	At 20°.
0	N/0	1·00	2·10
2·925	N/20	2·32	2·70
5·850	N/10	2·79	3·15
11·70	N/5	3·41	3·75
14·62	N/4	3·68	4·00
29·25	N/2	4·40	4·70
58·50	N	5·72	6·00
87·75	N½	6·58	6·85
102·3	N¼	6·90	7·15
117·0	2N	7·10	7·30
131·6	2N½	7·20 (max.)	7·30 (max.)
146·2	2N¾	7·10	7·13
160·8	2N¾	7·00	7·05
175·6	3N	6·80	6·80
204·7	3N½	6·30	6·30
234·0	4N	5·90	5·90
263·2	4N½	5·50	5·52
292·6	5N	5·30	5·30

These figures form two regular curves very close together.

We see that:—1. As the proportion of NaCl increases, the solubility increases at first rapidly, then slowly until it reaches a maximum.

2. This maximum corresponds to about 130 grms. per litre (about 2N4). It appears to depend to a slight extent on the temperature. The observations were more numerous in the neighbourhood of the maximum so as to determine its position with accuracy.

3. In solutions only slightly charged with NaCl, the solubility varies but little with the temperature.

4. At saturation-point the solubility is decidedly greater than it is in pure water.

The figures given above differ considerably from those given by M. Cloez (*loc. cit.*), but they agree very closely with those given by F. Clameron (*Bull. Soc. Chim.*, vol. xxviii., p. 50), who found a maximum of 7.5 grms. of anhydrous SO_4Ca at 23° , in solutions containing from 135 to 140 grms. of NaCl per litre.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 9.

COLORIMETRIC ESTIMATION OF BISMUTH.

By PAUL PLANÈS.

WHEN an acid aqueous solution of a salt of bismuth is treated with an aqueous solution of iodide of potassium, we obtain a brown precipitate of iodide of bismuth.

If, on the other hand, we add the bismuthic solution to the solution of iodide of potassium, at first we do not obtain any precipitate, but only a more or less deeply coloured orange-yellow colouration, and it is only on adding an excess of the bismuthic solution that we observe the formation of a precipitate of BiI_3 .

We have observed that if, when operating as in the first case, we take the precaution of adding its own volume of glycerin at 30° to the bismuthic solution, the subsequent addition of iodide of potassium does not cause any precipitate, but only an orange colouration; the BiI_3 remains in solution owing to the glycerin; in the same way the addition of glycerin at 30° in the second case prevents any precipitation of BiI_3 , no matter what excess of bismuthic solution there may be.

The glycerin plays a double part:—

a. It prevents the precipitation of BiI_3 ;

b. When present in sufficient proportion, it prevents the dissociation of the salts of bismuth by dilution with water, which enables us to work with very slightly acid bismuthic solutions, and reduces to a minimum the chances of the dissociation of the iodides by the nitric acid.

We have observed, further, that the orange-yellow colouration obtained under the above optimal conditions was proportional:—

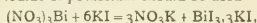
1. To the amount of KI added in excess to the bismuthic solution;

2. To the amount of bismuthic solution added in excess to the solution of KI.

Thus, by the mixture of two colourless solutions, we obtain a perfectly limpid coloured solution, and there is a definite relation between the amounts of the substances mixed and the intensities of the corresponding colourations; these elements are sufficient for a colorimetric estimation.

For the estimation of bismuth in any form, it is necessary to have at our disposal a standard solution of bismuth containing a considerable amount of glycerin, and a titrated solution of potassic iodide, also containing a large amount of glycerin.

To estimate the strength of the standard bismuth solution, we have examined the reaction in which the maximum amount of iodide of potassium should be used—



and according to which, one molecule of neutral nitrate of bismuth corresponds to six molecules of potassic iodide; in other words, 208 grms. of Bi corresponds to 996 grms. of KI; or again, 1 gm. of Bi corresponds to 4.79 grms. of KI.

We adopted therefore a standard solution of bismuth at 1/100th, and a titrated solution of potassic iodide at 5/100ths.

Preparation of the Standard Solution of Bismuth at 1/100th.—Our first care was to obtain pure bismuth. For this purpose, following the instructions given by Des-camps, we dissolved commercial bismuth in nitric acid, (this transformed the tin present into insoluble metastannic acid); decanted, added an excess of ammonia (this precipitated the oxide of bismuth, and dissolved the Ag_2O and CuO); treated the oxide of bismuth with a 2 per cent solution of soda (this removed the Pb and As); dissolved 4 parts of the oxide in 1 part of nitric acid, and precipitated with distilled water in the form of basic nitrate of bismuth. The sub-nitrate obtained in this manner, after various corroborative assays to confirm the absence of impurities, (Marsh's apparatus, H_2SO_4 , NH_3 , &c.), was reduced by charcoal after being thoroughly well mixed, and we used the ingot thus obtained, after having once more verified its purity.

Method of Procedure.—Dissolve 1 gm. (accurately weighed) of the pure bismuth in a mixture of 3 c.c. of official nitric acid and 2.8 c.c. of distilled water, following the instructions in the Codex, and after solution make up to 100 c.c. with glycerin at 30° . The standard solution thus obtained does not change.

Preparation of the Titrated Solution of Iodide of Potassium at 5/100ths.—Dissolve 3 grms. of pure KI (obtained according to the instructions given in the Codex, but using CO_3K_2 instead of KOH—the CO_3K_2 itself should be prepared by the calcination of the purified acid tartrate of potassium) in 5 c.c. of distilled water and make up to 100 c.c. with glycerin at 30° . This should be kept away from the light in a yellow glass bottle.

Applications.—As an example, we will take the titration of a commercial sub-nitrate of bismuth.

It is evident that, to facilitate the comparisons, we should try to obtain a solution of the sub-nitrate, containing a proportion of bismuth similar to that present in an equal volume of the standard solution.

Now a normal sub-nitrate of bismuth should contain 76.78 per cent of BiO_3 ; that is to say, 68.83 per cent of pure bismuth; from which it results by a very simple calculation, that to obtain the solution in question we must take 1.45 grms. of the sub-nitrate and make the necessary solution up to 100 c.c.

Method of Procedure.—Pour 10 c.c. of the standard solution of bismuth into a 50 c.c. matrass, add 10 c.c. of the titrated solution of KI, and make up to 50 c.c. with—

Glycerin at 30° + distilled water, *q.s.*

In a second matrass of 50 c.c. capacity, place 0.15 gm. of the sub-nitrate of bismuth under examination dissolved in dilute nitric acid, add 10 c.c. of glycerin at 30° , then 10 c.c. of the titrated KI, and make up to 50 c.c. with—

Glycerin at 30° + distilled water, *q.s.*

There then only remains to make the colorimetric examination either by varying the thickness of the solution or by dilution. Bismuth in any form can always be brought to the state of bismuthic nitrate; therefore the above method is applicable to all the mineral or organic derivatives of bismuth.

It may be conceived that inversely it is possible to effect the titration of an iodide in solution, by means of a titrated solution of bismuth, so long as there is a large excess of glycerin present to prevent the precipitation of BiI_3 , as we remarked at the commencement of this paper.

Further, certain substances which have very definite relations with the iodides, may be estimated indirectly by this method.

In a future paper we shall describe the method of working for the estimation of each individual bismuthic derivative, and inversely of the iodides and substances having precise relations with them.—*Journ. de Pharm. et de Chim.*, Series 6, vol. xviii., No. 9.

NEW DESIGNS FOR CHEMICAL BALANCES.

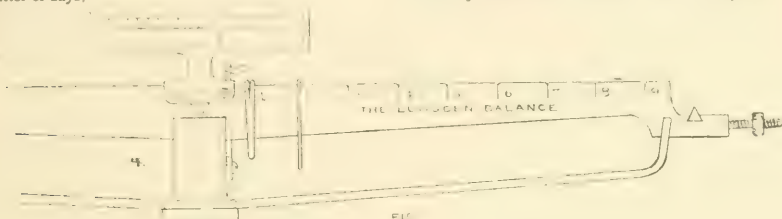
By JOHN S. LUMSDEN D.Sc., Ph.D.

TEACHERS of elementary classes in chemistry and physics are greatly troubled by the destruction and loss of the smaller weights when students are performing experiments requiring the use of a balance. The balances used in schools and by beginners in colleges weigh accurately to a centigram., and with approximate accuracy to a milligram., yet many types have no graduations on the beams, and students must employ the very smallest weights. There is in consequence great expenditure of time and the duration of the usefulness of the milligram. weights is only a matter of days.

a 5 centigram. ring rider is employed, which rests on the central division when not in use. This auxiliary beam is an important feature. It ensures in every case that the student will attempt to weigh to a milligram., and a 5 centigram. rider is so strong that there is little danger of it being destroyed. If there is no objection to the use of decigram. weights, the two lighter riders, one on each beam, make a very simple system, and by having a loop on the riders, they could be moved when the balance is in a case by a sliding shifter.

The use of a balance of this kind will effect a saving of time, it will be as accurate and only slightly dearer than the balances presently employed, and the weights will never get lost.

Mr. S. J. Shand, a student in the laboratory of Uni-



The annexed diagram (Fig. 1) shows a school balance, in the use of which no free weights smaller than a gm. are employed, the lesser values down to milligrams being got by rider weights of a ring shape which are permanently kept on the balance.

The right arm of the beam has ten divisions, and decigrams are found by a gm. rider, and centigrams by a decigram. rider. These riders when not in use are supported on a hook which is screwed to the brass block on

versity College, Dundee, has devised an ingenious method of graduating a balance which is of interest and may be of practical value.

In Fig. 3 a beam is shown graduated into ten parts on each side of the centre, but the numbers on both sides read from left to right. The first division on the right is marked 0 and the first division on the left is marked 9. A decigram. rider placed on 0 to the right balances a centigram. rider on 0 to the left. This is the position of the riders when the balance is at rest.

If the decigram. rider is moved along to division 5, that is, $\frac{1}{2}$ from the centre, the other rider remaining as before, the weight is 0.05 gm. If now the centigram. rider is brought towards the right, the weight increases each division by 0.001 gm., and when the rider rests on 6, the weight is 0.056 gm., as shown on Fig. 4.

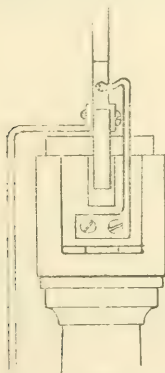
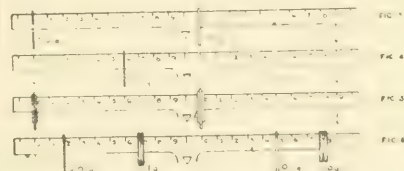


FIG 2

the top of the centre rod, as shown in Fig. 2. In order to make weighings such as 0.11 or 0.22 gm. possible, a notch is made on the upper part of the heavier rider, so that the lighter one, which has a greater diameter, may rest on the top of it. A light aluminium auxiliary beam, one-fifth of the length of the main beam, is used to measure milligrams. It is divided on each side of the centre into ten parts and



A more complete example is got by using four riders, viz.: 0.01, 0.1, 1, and 10 grms. The zero position is shown on Fig. 5 and a weight of 8.752 grms. on Fig. 6.

The substance to be weighed having been placed on the left pan of the balance, the 10 grms. rider on the right arm is moved along and found to be too heavy on 9; it is therefore placed on 8. The 1 gm. rider on the left arm is then shifted forward, and being too heavy on 8 it is placed on 7. Similarly the 0.1 gm. rider is placed on 5 to the right and the 0.01 gm. rider on 2 to the left. The reading taken in the order of the weights of the riders is thus 8.752 grms.

A balance graduated in this way and using centigram. and decigram. riders would be very good for assay work, and

weighing machines for ordinary commercial purposes might be devised to work with heavy riders instead of free weights.

University College, Dundee

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 22, November 30, 1903.

Fusibility of Mixtures of Bismuth Protosulphide and Silver Sulphide, Bismuth Protosulphide and Antimony Sulphide.—H. Pelabon.—When silver sulphide and bismuth protosulphide are melted together a homogeneous liquid is produced. The temperature at which solidification begins can be easily determined exactly. A curve of fusibility of such mixtures can be constructed, having for ordinates the temperature of solidification, and for abscissae values corresponding to the proportion of the mass of silver sulphide to the total mass of the mixture. In the same manner the author examines mixtures of bismuth protosulphide and antimony sulphide with a view to determining the curve of fusibility.

Influences Accelerating or Retarding the Action of Manganese considered as a Metallic Ferment.—A. Trillat.—The author makes various experiments on the action of manganese employed as a metallic ferment. He finds that to render the metal active for the conditions under which he is working, the medium to be oxidised must contain an alkali or an alkaline earth salt. For the same quantity of alkali increasing proportions of manganese retard the action, as in the case of diastatic phenomena. The progress of the reaction can be hindered by the presence of traces of certain substances. Indeed, in order that manganese may produce the maximum effect in a medium in a given time a number of conditions have to be fulfilled.

Systematic Alcoylation of Arsenic.—V. Auger.—Up to the present time no method has been discovered of attaching one, two, or three alcoyl groups severally to the molecule of arsenic. Cahour's method consists in heating the metalloid with an alcoholic iodide. This immediately results in the formation of a mixture of tri- and tetra-substituted derivatives, whilst Meyer's method apparently only produces a single product, sodium methylarsinate. It is, however, in generalising this latter reaction that the author arrives at the systematic introduction of alcoholic groups into arsenic compounds.

Separation of Iodine from Alkaline Halogen Salts of Iodine, Chlorine, and Bromine by the Transformation into Iodic Acid, and a Method of preparation of Pure Iodine.—H. Baubigny and P. Rivals.—In order to separate iodine from a mixture of iodides, chlorides, and bromides, the authors take advantage of the easy oxidisability of iodine, and transform the whole of it into iodic acid, a stable and non-volatile body. They then successively separate the bromine and the chlorine by distillation. This method has given excellent results. Permanganate instantly oxidises iodides to iodesates. The authors also evolve from this separation a method of obtaining perfectly pure iodine.

MISCELLANEOUS.

King's College, London.—Evening Course in Bacteriology.—A course in Practical and Clinical Bacteriology will be held every Monday evening from 6.30 to 8.30, commencing Monday, January 11th, and ending Monday, March 8th. The course will consist of lectures, demonstrations, and practical work. In the latter, the members of the class will make for themselves permanent preparations of the chief pathogenic micro-organisms, and will carry out the principal manipulations employed in bacteriological investigations. The fee will be £3 3s., including all materials and the use of a

microscope. Names must be sent in as soon as possible to the Secretary, or to Prof. Hewlett, as the class will not be held if less than six students join. Special classes are formed for Institute of Chemistry examinations.

ERRATUM.—In last issue, p. 317, col. 2, line 6 from top, for "nickel and zinc" read "nickel and cadmium."

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Society of Chemical Industry, 8. "On the Defects of Uncarbonated Water-gas as Fuel for 'Laboratory Use,'" by Dr. Chikashige. "The Rapid Estimation of Mercury by means of Hypophosphorous Acid," by B. F. Howard. "The Determination of Moisture in Nitro-glycerin Explosives," by Arthur Marshall.

TUESDAY, 5th.—Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "On Exotic Animals," by Prof. Rev. Luke, M.A., D.D., F.R.S.

**THE SIR JOHN CASS TECHNICAL INSTITUTE,
JEWRY STREET, ALDGATE, E.C.**

Principal—CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.

EVENING CLASSES IN CHEMISTRY, METALLURGY, PHYSICS, and MATHEMATICS.

Designed to meet the requirements of those engaged in CHEMICAL, METALLURGICAL, and ELECTRICAL INDUSTRIES, and in trades associated therewith.

Every facility for Special and Advanced Practical Work in well-equipped Laboratories.

CHEMISTRY	{ CHARLES A. KOHN, M.Sc., Ph.D., F.I.C., and G. SENTER, B.Sc., Ph.D.
PHYSICS	R. S. WILLOWS, D.Sc., B.A.
METALLURGY	C. O. BARNISTER, Assoc.R.S.M.
MATHEMATICS	G. W. KAYE, B.Sc.

CLASSES IN METALLURGY.

GENERAL METALLURGY.
THE METALLURGY OF GOLD AND SILVER.
METALLOGRAPHY, including PYROMETRIC WORK.
ASSAYING.

ANALYTICAL CHEMISTRY.

Including E.L.E., TITRIMETRIC and GAS ANALYSIS.

Each Course of Lectures will be accompanied by suitable Laboratory Work.

GLASS BLOWING.

Two Courses of Instruction will be given during the Lent Term by Mr. A. C. COSBOR.

New TERM begins **MONDAY, JANUARY 4th,**
1904.

The Institute is readily accessible, and near to Fenchurch Street, Liverpool Street, Broad Street, and Metropolitan Railway Stations.

For details of the Classes apply at the Office of the Institute, or by letter to the PRINCIPAL.

W. H. DAVISON, M.A.,
Clerk to the Governing Body.

MERCK'S

Complete OF FINE . . .
Catalogue CHEMICALS

(Autumn 1903 Issue) NOW READY.

Write at once to—
E. MERCK,
16, JEWRY STREET, LONDON, E.C.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2302.

ON A PRINCIPAL CAUSE OF THE SALTNESSE OF THE DEAD SEA.*

By WILLIAM ACKROYD, F.I.C., F.C.S., &c.,
Public Analyst for Halifax.

THE saltiness of the Dead Sea has been ascribed to two causes:—(1) The accumulation of chlorides derived from the rocks of the Holy Land by solvent denudation, and (2) the cutting off of an arm of the Red Sea by the rising of Palestine in past ages, with, in each case, the subsequent concentration of the solution by evaporation (Hull, *The Phys. Geol. of Arabia Petraea and Palestine*, pp. 119 and 120). There is a third cause, which is probably more important than either, viz., the atmospheric transportation of salt from the Mediterranean. The circulation of salt is a reality which must be taken into account. Brought from the sea by winds and falling in the rain, the salt is carried back to the sea by rivers, except in cases of inland lakes without outlet, where the saline solution remains for evaporation, and I have shown that in the case of an inland Pennine reservoir such a cause would produce a water as salt as that of the Dead Sea in a fraction of the time usually assigned to the Pleistocene Age (*Geol. Mag.*, October, 1901, p. 446; also compare J. G. Goodchild, *Trans. Geol. Soc. of Glasgow*, 1898, vol. xi., Part I., p. 84).

For the purpose of the present paper analyses of rain-water from the Holy Land are wanting; as, however, they are not at present available, I assume that the rain, like that of other lands, is charged with salt to a degree which varies in a direct manner with the velocity of the winds coming from the sea; it then only remains to show that the rocks are not abnormally salt bearing (*Proceedings of the Yorks. Geol. and Polytechnic Soc.*, vol. xiv., Part III., pp. 403–408).

I have had forwarded to me by the Palestine Exploration Fund specimens of the rocks on which Jerusalem is built as samples of Palestine rocks. They are limestones of various compositions, and the amount of common salt, calculated from the chlorine I have found in them, is given in the following table:—

Description of limestone.	Per cent of chlorine.	Calculated per cent of common salt.
1. Kakule	0.025	0.041
2. Nahr	0.001	0.002
3. Meleke	0.006	0.010
4. Misse (yehudi) ..	0.005	0.008
5. Misse (helu) ..	0.0015	0.002
6. Misse (achmar) ..	0.001	0.002
Average	—	0.01

The salt contained in these rocks, except in the case of Kakule limestone, is no greater in amount than that found in the limestones of other lands which similarly approximate to a general average of 0.01 per cent of chlorine. This amount of chlorine would be quite inadequate to account for the salt in the Dead Sea. By a technical argument, based on the amount of chlorine in a rock and its rate of denudation, I have shown that the salt yielded to rivers from this source is not a ninety-ninth of that which has been supplied by rain-water (CHEMICAL NEWS, vol. lxxxiii., p. 301, and *Geol. Mag.*, October, 1901, p. 447). Nor would the saltiness of the Dead Sea be fully accounted for if a marine area had been cut off during the rising of the land, as the initial saltiness thus acquired

* From the Quarterly Statement of the Palestine Exploration Fund.

would only be about a fourth of that subsequently attained to, and moreover in this condition of saturation it has been for an unknown length of time continuously precipitating its excess of salt. Hull observes (*op. cit.*, p. 120):—"The increase of saltiness in the waters of the Dead Sea has probably been very slow, and dates back from its earliest condition when its waters stretched for a distance of about 200 miles from north to south. While the uprising of the land and the sinking down of the Jordan Arabah depression were in progress during the Myocene period, some of the waters of the outer ocean, themselves salt, were probably enclosed and retained; but from the occurrence of the shells in the marls in the Arabah Valley, it would appear that when the waters of the great inland lake were at their maximum elevation, they were sufficiently fresh to allow of the presence of molluscan life. This would be during the Pluvial epoch, but at the stage represented by the salt beds of Jebel Usdum, the waters, which were then 600 feet higher than at present, must have been saturated with chloride of sodium." One may add that the intensity of meteorological conditions in the past geological history of Palestine have been much more severe than those now obtaining, and the atmospheric transportation of salt would be correspondingly greater (Tristram, "The Land of Israel," p. 320). Some of the salt then accumulated has been left by the dwindling waters of the Dead Sea in areas to the north and south, notably in Jebel Usdum, and the highly brackish rivulets which come from these neighbourhoods now are but contributing again what long ago came from more distant sources.

I find confirmation of the theory in the fact that the ratio of the chlorine to the bromide in the waters of the Dead Sea is approximately the same as that for these two elements in the Mediterranean Sea (*Proceedings of the Yorks. Geol. and Polytechnic Soc.*, 1902, vol. xiv., Part III., p. 408).

In conclusion, I have to offer my best thanks to Mr. Walter Morrison, J.P., of Malham, and Mr. George Armstrong for the privilege of having been enabled to examine the rocks from Palestine which are mentioned in this paper.

ACTION OF SOME GASES ON BARIUM-AMMONIUM.

By MM. GUNTZ and MENTKE.

WE have examined the action of several gases on the solution of barium-ammonium in liquid ammonia, notably that of oxygen, of carbonic oxide, and of binoxide of nitrogen.

The pure dry gas with which the experiment is to be made, is collected in a mercury gas-holder, and for the purpose of complete desiccation it remains in contact with phosphoric anhydride contained in a tube, τ , connected with a manometer. By pouring mercury into a branch tube of the gas-holder, any desired pressure can be attained, and the stop-cock turned off to retain it.

To carry out an experiment, the solution of barium-ammonium is prepared in a suitable vessel, A , cooled to -50° , to bring the tension of the ammonia below that of the gas contained in the tube, τ , and the tap is opened, making communication between the tube τ and the vessel A . When a sufficient quantity of gas is estimated to have passed, the tap is turned off. The volume of τ having been previously determined, it suffices to read off the pressure on the manometer before and after the introduction of the gas into the vessel, to calculate the actual quantity brought into the presence of the ammonium.

When the reaction is terminated, the vessel, A , is allowed to return to the ordinary temperature; the liquid ammonia volatilises and escapes by a side tube, carrying off also the gases which have not reacted, or those which may have been produced during the experiment. It is easy to collect these gases for analysis.

Action of Oxygen.

By bringing oxygen into contact with the solution of barium-ammonium prepared in a small flask, this gas is absorbed; it produces a white gelatinous precipitate, remaining in suspension in the liquid ammonia. The reaction is slow at -50° , and the last portions of the barium-ammonium are very difficult to decompose on account of its slight solubility in ammonia at this temperature. The gelatinous precipitate formed encloses the non-dissolved ammonia in bubbles, and prevents it coming in contact with the oxygen.

At a higher temperature, and especially when operating with an excess of oxygen, the blue solution is decolorised very rapidly.

When the reaction is complete, the ammonia is entirely removed; a white amorphous powder is then deposited, which, when treated with dilute hydrochloric acid, is dissolved without the evolution of any gas, giving a solution containing peroxide of hydrogen and no ammonia.

Whatever the method of procedure adopted, and the temperature of the experiment, the products obtained have practically identical compositions.

The barium was weighed before the reaction; the peroxide formed is estimated by permanganate, and the active oxygen in the solution calculated into binoxide of barium, BaO_2 .

At -50° , by adding oxygen gradually as it is absorbed, and stopping the experiment after the decolorisation of the solution, we find 9.07 of barium in the form of BaO_2 and 90.9 in the form of BaO .

At -35° , the oxygen being in excess and remaining in contact with the gelatinous product after decolorisation, the composition was 7.5 of barium in the form of BaO_2 and 92.5 in the form of BaO .

Thus, contrary to what takes place with the alkaline ammonias, the reaction of the oxygen on the barium only gives a small quantity of the higher oxide.

Action of Carbonic Oxide.

The action of carbonic oxide on barium varies according to the conditions of the experiment.

When we heat the metal in a current of this gas, no attack takes place below 500° . At this temperature it becomes black, but the change is only superficial. The black layer which covers the metal gives off acetylene in the presence of water; thus there is a formation of carbide of barium.

The action of carbonic oxide on the ammoniacal solution of barium-ammonium is quite different. At -50° it takes place very easily, and the decolorisation is even more rapid than with oxygen. A yellow gelatinous precipitate is formed, which is deposited, on the removal of the ammonia, in the form of a yellow amorphous powder.

We determined the composition of this body by weighing the substance formed by the fixation of the carbonic oxide by a known weight of barium; this is easily done. Our results were:—

	Found	Theory for $\text{Ba}(\text{CO})_2$.
Ba	72.1	71.05
CO	27.9	28.95

We have not been able to make an analysis of the sub-carbonate of barium, as this body decomposes with loss of heat, if only a little air or a trace of moisture is allowed to enter the vessel containing it.

The product of this decomposition is completely soluble in water, and gives a yellow solution that we have not yet examined.

If barium sub-carbonate is heated *in vacuo*, it becomes brown at about 100° ; at about 250° it decomposes with incandescence, the mass swells up, but without any evolution of gas or explosion. The residue consists of baryta, carbonate of barium, and finely divided carbon.

The product which has undergone the action of the air is also decomposed, but at a higher temperature, giving the same substances.

The reaction of the decomposition of the sub-carbonate of barium may, consequently, be expressed in the same manner as that of the sub-carbonate of sodium, $2\text{Ba}(\text{CO})_2 = \text{BaO} + \text{BaCO}_3 + 3\text{C}$.

Action of Bin oxide of Nitrogen.

Bin oxide of nitrogen reacts easily on barium-ammonium. The gelatinous precipitate produced by this reaction is deposited in the form of a white powder on the evaporation of the ammonia.

We have observed the formation of the hyponitrite of barium, $\text{Ba}(\text{NO})_2$; this was recognised by its silver salt, after having allowed the white powder to become slowly hydrated by contact with steam before dissolving it, as it decomposes with the evolution of protoxide of nitrogen in the presence of a drop of water.

Thus the solution of barium-ammonium behaves like that of sodium.

We intend proceeding with the examination of the other compounds which may be obtained by means of this solution.

We may add that barium-ammonium can be also prepared by the action of liquid ammonia on 60 per cent amalgam. In this case there remains an amalgam very poor in barium.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 12.

THE DETERMINATION OF BENZENE IN
ILLUMINATING GAS.*

By L. M. DENNIS and J. G. O'NEILL.

IN 1891, Hempel and Dennis described a method for the volumetric determination of certain hydrocarbons that are usually present in illuminating gas (*Ber. d. Chem. Ges.* xxiv., 1162). Up to that time, all hydrocarbons in this product, with the exception of methane, had been determined by absorption with fuming sulphuric acid, and had been classed under the general term "heavy hydrocarbons." It is true that Bunsen ("Gasometrische Methoden," Second Edition, 1877, p. 142) gives an analysis of illuminating gas in which the percentages of benzene, ethylene, and propylene are stated, but the amounts of these three gases were calculated by means of equations from the results of explosions with air and oxygen, and the calculation was based upon the assumption that the heavy hydrocarbons in the gas consisted only of ethylene, propylene, and benzene. It was ascertained by Hempel and Dennis that certain hydrocarbons, such as benzene and naphthalene, could be removed, in part at least, by means of absolute alcohol, the remainder of the heavy hydrocarbons being then absorbed by fuming sulphuric acid, and the methane being finally determined by explosion or combustion. In 1894, Noyes and Blinks adapted the method of Hempel and Dennis to the Bunte burette (*Journ. Am. Chem. Soc.*, xvi., 697).

Recent work in this laboratory, however, has shown that while the absorption of benzene by means of alcohol may sometimes give agreeing results, the removal of the benzene is usually by no means complete, and the results, at times, show wide variations. The following analyses are given in confirmation of this statement. Air was drawn into a Hempel burette containing water as the confining liquid, and was measured. It was then passed into a gas pipette containing benzene, and was drawn back into the burette, and the increase in volume noted. The mixture of benzene and air was next passed into a pipette containing mercury and 3 c.c. of absolute alcohol, and was shaken for three minutes in contact with the alcohol. The residue was then drawn back into the burette, and was passed into a pipette filled with water, and was shaken with that liquid for three minutes to remove the vapour of

* From the *Journal of the American Chemical Society*, xxv., No. 5.

alcohol. The gas was now drawn back into the burette and measured. The results were:—

TABLE I.

	I.	II.	III.
	C.c.	C.c.	C.c.
Air taken	67.0	50.0	52.2
Air plus benzene (C ₆ H ₆) ..	73.0	54.0	57.0
After shaking with alcohol ..	69.0	51.8	54.2
After shaking with water ..	68.4	51.4	53.7
Benzene taken	6.0	4.0	4.8
Benzene found	4.6	2.6	3.3

Experiments were next tried to ascertain whether repeated treatment with alcohol would remove all of the benzene, and, as will be seen from the table below, it appears that this reagent is unable to remove benzene completely from mixtures of that substance with air.

TABLE II.

	I.	II.	III.	IV.	V.
	C.c.	C.c.	C.c.	C.c.	C.c.
Air taken	58.6	60.1	63.0	56.8	67.9
Air plus benzene	62.8	64.6	67.0	61.0	72.8
After shaking with alcohol ..	59.8	61.6	63.8	57.8	69.0
After shaking with water ..	59.4	61.1	63.8	57.6	68.8
After second shaking with alcohol	59.2			—	—
After second shaking with water	59.1			—	—
After third shaking with alcohol	59.1			—	—
After third shaking with water	59.1			—	—
After passing residue into fuming sulphuric acid and then into the potassium hydroxide pipette ..	58.7	60.2	62.9	—	—

It was therefore apparent from these results that for the complete and speedy removal of benzene from illuminating gas some absorbent other than absolute alcohol must be employed.

In 1897, Hofmann and Küspert described (*Zeit. Anorg. Chem.*, xv., 204) certain compounds of hydrocarbons with metallic salts, and stated that when illuminating gas acts upon a mixture of nickel hydroxide and aqua ammonia, there results a compound of nickel cyanide with ammonia and benzene, Ni(CN)₂.NH₃.C₆H₆. This statement led the authors of the present paper to examine into the action of an ammoniacal nickel solution upon benzene with the view to ascertaining whether a method could be developed for the volumetric determination of the benzene that is present in the form of vapour in gas mixtures. Sufficient of the absorbent to fill a Hempel simple absorption pipette (about 150 c.c.) was prepared by dissolving 25 grms. of crystalline nickel nitrate, Ni(NO₃)₂.6H₂O, in 50 c.c. of water and adding 50 c.c. of strong aqua ammonia. The solution was allowed to cool, was decanted from any salt that separated out, and strong aqua ammonia was then added until the volume amounted to 150 c.c. The solution loses its efficiency if diluted with water, and its absorptive power is greatly diminished if nickel hydroxide is present in suspension. The analytical results given in this paper were obtained with the reagent prepared in this manner. Experiments showed that this solution absorbed nothing from air, but that when shaken with a volume of air it gave off a small amount of ammonia gas. In the first series of experiments it was sought to remove this ammonia by passing the gas mixture into a Hempel pipette filled with water, but, since this did not entirely remove the ammonia, it was found necessary to use in place of the water a 5 per cent solution of sulphuric acid.

Later experiments made in this laboratory by Mr. W. C.

Geer have shown that it is possible to prepare the reagent in such manner as to do away with the necessity of the treatment of the gas mixture with dilute sulphuric acid. The method of preparation of the reagent is as follows:—Forty grms. of nickel nitrate are dissolved in 160 c.c. of water to which has been added 2 c.c. of nitric acid of specific gravity 1.44. This solution is poured slowly with constant stirring into 100 c.c. of ammonium hydroxide, specific gravity 0.908. The resulting deep blue solution is used in the absorption. It has a very slight tinge of lavender. The odour of ammonia is noticeable, but is not strong. The few analyses that have been made with the reagent prepared in this manner indicate that it is similar in action to that prepared as above described, and that it is equally efficient. It should, however, be more thoroughly tested before complete reliance is placed upon it.

(To be continued.)

THE BEHAVIOUR OF CERIU, LANTHANU, NEODYMIU, PRASEODYMIU, THORIUM, AND ZIRCONIU TOWARD ORGANIC BASES.*

By BURT LAWS HARTWELL.

An investigation along these lines seemed to promise well because of the success which Jefferson met while prosecuting a similar study with a limited number of aromatic bases (*Four. Am. Chem. Soc.*, xxiv., 540). It was hoped that some organic base would be found, among the large number to be tried, which would lead to the separation of thorium and zirconium, or failing in this, that a method would be disclosed by which these two elements could be separated from cerium, lanthanum, neodymium, and praseodymium.

Large quantities of thorium and zirconium nitrates were prepared from the mineral thorite and zircon. Numerous qualitative tests were made and the solvents for the bases were, in most cases, water and alcohol, or mixtures of these two, depending upon the solubility of the base. In some instances ether was added to advantage. Alcohol, above a certain strength, precipitated the thorium and zirconium nitrate solutions, so that this point had to be constantly considered during the testing. The salt solution was usually added in small quantities at a time to the solution containing a liberal amount of the organic base. Heat was applied, if precipitation did not occur in the cold. The solutions were not permitted to stand for long periods, as it was thought that differences which did not manifest themselves readily, under ordinary conditions, would scarcely indicate the probability of practical quantitative separations.

The bases studied in this investigation were obtained from Kahlbaum. Those employed by Jefferson were usually omitted here (*loc. cit.*)

The bases of the first and second groups were manifestly unsuited for the purpose in mind. Those of the third and fourth groups showing differences in deportment with the several elements under consideration were given more particular attention, while those which were insoluble in dilute alcoholic solutions were placed to one side. The following paragraphs record the observations made with the several bodies which seemed best adapted for quantitative separations.

Thorium and Zirconium with the Chloranilines.—The different behaviours of the chloranilines substantiate the views held regarding their relative basicity (van't Hoff's "Lectures on Theoretical and Physical Chemistry," vol. ii., p. 102). *o*-Chloraniline did not precipitate thorium or zirconium. *m*-Chloraniline precipitated zirconium in the cold, but with thorium heat was required to produce

* Contributions from the John Harrison Laboratory of Chemistry. (From author's thesis for Ph.D. degree.) From the *Journal of the American Chemical Society*, xxv., No. 11.

Reagents which Produced no Precipitate with Salts of any one of the Six Elements.

Benzylaniline.	<i>o</i> -Nitraniline.
Dimethylnitrosamine.	<i>o</i> -Chloraniline.
<i>p</i> -Nitraniline.	Piperine.
<i>p</i> -Nitrophenylhydrazine.	Succinimide.
Dipropylnitrosamine.	Tetranitromethylamine.
<i>m</i> -Nitraniline.	

Reagents which Caused Precipitates with Salts of all Six of the Elements.

Allylamine.	Monooxylamine.
Benzylmethylamine.	Monethylamine.
Bornylamine.	Monomethylamine.
Camphylamine.	Monopropylamine.
Diamylamine.	Neurine.
Dibenzylamine.	Normal butylamine.
Diethylamine.	Normaldiethylamine.
Dimethylamine.	Propylenediamine.
Dipropylamine.	Tetretethylammonium hy-
Ethylenediamine.	droxide.
Heptylamine.	Tetramethylammonium hy-
Hexylamine.	droxide.
Isobutylamine.	Triethylamine.
Isotributylamine.	Trimethylamine.
Isodibutylamine.	Tripropylamine.

Reagents which Precipitated only Thorium and Zirconium.

Benzidine.	Isoquinoline.
<i>m</i> -Bromaniline.	α -Picoline.
<i>p</i> -Bromaniline.	<i>p</i> -Toluidine.
<i>p</i> -Bromophenylhydrazine.	<i>m</i> -Toluylenediamine.
<i>p</i> -Chloraniline.	Tribenzylamine.

Reagents not Included in the Preceding Groups and whose Reactions are mentioned upon Succeeding Pages.

<i>m</i> -Chloraniline.	β -Naphthylamine.
Diethylamine.	Tetrahydroquinoline.
Hexamethylenetetramine.	<i>m</i> -Toluidine.
Monethylamine.	<i>o</i> -Xylidine.
Monomethylamine.	<i>p</i> -Xylidine.
α -Naphthylamine.	

precipitation, while *p*-chloraniline precipitated the solutions of both elements, even in the cold. Solutions of cerium, lanthanum, neodymium, and praseodymium salts were not affected by these reagents.

Zirconium and Thorium with m-Chloraniline.—Much work was done upon *m*-chloraniline to arrive at the proper conditions in the strength of alcohol and temperature favourable to the complete precipitation of the zirconium solutions, and at the same time to leave the thorium salt unprecipitated. A solution containing equal parts of water and commercial alcohol was found most satisfactory. At a temperature of 60–70°, this solvent containing *m*-chloraniline occasioned no precipitation in solutions of thorium nitrate, while in zirconium nitrate solutions it precipitated 0.0995 grm., 0.0988 grm., 0.0990 grm., and 0.0988 grm. of zirconium oxide, instead of 0.0995 grm. obtained by ammonia or 0.0993 grm. by direct evaporation and ignition. On repeating the experiment with a mixture of the thorium and zirconium nitrates, both elements were completely precipitated.

Thorium and Zirconium with Hexamethylenetetramine Formin.—Formin in the qualitative tests showed a marked difference in behaviour. Thus a thorium solution, after its addition, stood forty-two hours at room temperature without the appearance of a precipitate. Upon adding the zirconium nitrate solution, both hydroxides were precipitated completely.

α - and β -Naphthylamine, *m*-bromaniline, and *p*-bromophenylhydrazine precipitated zirconium solutions much more completely than those of thorium, but separations could not be effected by means of them. They reacted

indifferently with the salts of cerium, lanthanum, neodymium and praseodymium. *o*-Bromaniline was not tried at all in this investigation.

In a solution of the nitrates of zirconium and cerium, *m*-chloraniline precipitated 0.0532 grm. of zirconium oxide, instead of 0.0539 grm. obtained with ammonia water. *p*-Chloraniline precipitated 0.0536 grm., *m*-bromaniline 0.0524 grm., and β -naphthylamine 0.0533 grm. In the first three filtrates 0.0396 grm., 0.0400 grm., and 0.0396 grm. respectively, of cerium oxide were obtained, instead of the theoretical 0.0389 grm. In using *p*-chloraniline with a solution containing twice the quantities of zirconium and cerium oxide given above, a very satisfactory quantitative separation resulted.

In precipitating a mixture of zirconium and cerium salts with *p*-toluidine, 0.1341 grm. of zirconium oxide was found, while the theoretical amount present was 0.1347 grm. This same reagent added to a solution of thorium and cerium nitrates precipitated 0.1246 grm., 0.1236 grm., and 0.1261 grm., instead of 0.1247 grm.

While monomethylamine precipitated cerium solutions completely and apparently had no marked effect upon those of lanthanum, neodymium, and praseodymium, the attempts at quantitative separations were fruitless. Diethylamine precipitated cerium salts quite completely. The insolubility, however, of this reagent compelled the use of such large amounts of alcohol that serious difficulties arose. These were not overcome. A quantitative separation of cerium from lanthanum was made by means of tetrahydroquinoline. Two precipitations of the cerium were necessary.

o- and *p*-Xylidine, as well as monethylamine, precipitated cerium completely from its salt solutions. *m*-Toluidine seemed inadequate for this purpose.

(To be continued.)

Transactions of the American Electrochemical Society.—Fourth General Meeting, Niagara Falls, N.Y., September 17, 18, and 19, 1903. (Vol. iv.)—At the above meeting of the Society a number of interesting papers were read, among them being "Advances in Electro-metallurgy of Iron Production," by Marcus Ruthenberg; "Note on the Electro-metallurgy of Gold," by W. H. Walker; "Electrolytic Copper Refining," by W. D. Bancroft; "Efficiency of the Nickel-plating Tank," by O. W. Brown; "A New Type of Electrolytic Cell," by P. G. Salom; "On the supposed Electrolysis of Water Vapour," by F. A. Lidbury; "Theoretical Properties of Free Ions in Solutions," by E. F. Roerber; "Present Status of the Electrolytic Dissociation Theory," by W. D. Bancroft; and a general discussion of the "Theory of Electrolytic Dissociation."

Simplification of the Method for the Estimation of Zinc in the Form of Sulphide.—A. Thiel.—The method recommended by the author has for its object the elimination of the always long and tedious filtration of the sulphide. The solution of zinc is precipitated in the usual manner by sulphuretted hydrogen in the presence of acetate of ammonia. Boil for two minutes by direct heating over a gas flame. After the deposition of the precipitate, the clear liquid is decanted on to an ordinary filter. The residue is washed several times with boiling water charged with sulphuretted hydrogen; it is then passed into an Erlenmeyer flask of 50 c.c. capacity, and evaporated on the water-bath. The neck of the flask should be kept plunged in the steam. The ash of the filter is added to the residue, and the whole heated to 120° in a current of sulphuretted hydrogen; the operation is terminated by driving off the last traces of sulphur in a current of hydrogen. If the solution available for the precipitation of the zinc contains a large amount of alkali or alkaline earths, the precipitate should be re-dissolved, and the operation of precipitation repeated a second or even a third time. The results are very exact.—*Zeit. Anorg. Chem.*, vol. xxxiii., p. 1.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, December 16th, 1903.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. E. F. ARMSTRONG, H. J. W. BLISS, E. R. HUGHES, B. INGRAM, and C. MÜLLER were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alick Cole Benson, 33, Perham Road, West Kensington; Robert Gawler, M.Sc., 3, South View Terrace, Leeds; Leo Frank Guttman, Ph.D., 18, Aberdare Gardens, N.W.; Cyril Douglas McCourt, 52, Victoria Road, Clapham, S.W.; Benjamin L. Murray, 19, University Place, New York; Thomas Stewart Patterson, Ph.D., Lyddon Hall, Leeds; Alfred Shrubsole, 91, Holyhead Road, Coventry; Samuel John Smith, 41, Grafton Street, Dublin; Alfred Tingle, Ph.D., B.Sc., Shantung, China.

Of the following papers, those marked * were read.

*165. "The Relative Strengths of the Alkaline Hydroxides as to Ammonia as Measured by their Action on Cotarnine." By J. J. DOBBIE, A. LAUDER, and C. K. TINKLER.

The authors have shown (*Trans.*, 1903, lxxxiii., 598) that in aqueous solution, cotarnine has the "ammonium hydroxide" form, whereas in ethereal or chloroform solution it exists as a "carbinol."

These two forms are distinguished by having widely different and very characteristic absorption spectra (*loc. cit.*, Plate I., carbinol form; Plate II., ammonium hydroxide form).

When cotarnine in aqueous solution is acted on by sodium hydroxide or any other soluble base, it is converted into the carbinol form. The proportion of the cotarnine which undergoes this change depends on the amount of sodium hydroxide present, the change being practically complete when a milligram-molecule of cotarnine is dissolved in one litre of normal sodium hydroxide solution. After the addition of any given quantity of sodium hydroxide, a state of equilibrium is established almost instantaneously, and no further change takes place in moderately dilute solutions, even after several hours, provided that the temperature is kept constant. Each additional quantity of sodium hydroxide causes a further transformation of "ammonium hydroxide" into "carbinol" form. This change can be followed through all its phases by photographing the spectra of the solution after each addition of sodium hydroxide, the spectra obtained being in reality those of mixtures of the two modifications (*loc. cit.*, Plate III., Figs. 17-24), the relative amounts of which can be determined by comparing these photographs with a standard series obtained by photographing the spectra of solutions prepared by mixing the two forms of cotarnine in definite proportions. It is possible, therefore, to estimate the amount of change which any given quantity of sodium hydroxide produces in an aqueous solution of cotarnine, and to obtain a curve representing the effect of successive additions of the alkali.

The action of ammonia and of the hydroxides of lithium, sodium, potassium, barium, and calcium has been examined in this way. The curves for the first three hydroxides are nearly identical, from which it is inferred that, so far as their action on cotarnine is concerned, they have practically the same strength; those of the last two agree with one another, but differ slightly from the others, indicating a slight inferiority of strength, especially for the more concentrated solutions.

The curve for ammonia, which differs widely from those of the alkaline hydroxides, indicates that this base is much weaker than the latter substances.

DISCUSSION.

Mr. W. C. REYNOLDS expressed the hope that Prof. Dobbie will be able to investigate, in this connection, the

parent bases, hydrastine and narcotine, from which hydrastine and cortarnine are derived by oxidation. In the case of hydrastine, he had noticed the existence of two modifications, one variety melting at about 131-132°, and the other at a temperature somewhat above 140°. If either variety was dissolved in alcohol or acetone and the solvent removed at the temperature of the water-bath, the less fusible variety was obtained; but if the solution was allowed to evaporate spontaneously, or if a concentrated hot solution was cooled and then allowed to crystallise, the more fusible variety was obtained. The less fusible variety was always produced by the fractional precipitation by ammonia of the hydrastine salts.

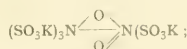
Moreover, if the temperature when in the neighbourhood of the melting-point was raised very slowly (about 1° per half-hour), the crystals appeared to change from the more fusible to the less fusible modification. The crystals which melted at 131-132° when heated in the ordinary manner, did not soften until the temperature was considerably above 140°, and then melted somewhat indefinitely.

Under similar conditions, both varieties seemed to have the same specific rotation in solution.

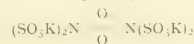
Similar changes were not observed in the case of the allied alkaloid, narcotine.

*166. "Peroxylaminesulphonates and Hydroxylaminetrisulphonates (Sulphazilates and Metasulphazilates)." By T. HAGA.

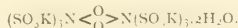
By oxidising potassium hydroxylaminedisulphonate, Fremy obtained the salts which he called sulphazilate and metasulphazilate. Claus re-named the former "oxysulphazotate," and formulated its constitution as—



the latter he called "trioxyazotate," giving it the formula $\text{O}:\text{N}(\text{SO}_3\text{K})_3 \cdot \text{H}_2\text{O}$. Raschig changed these formulæ into—

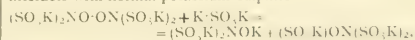


and—

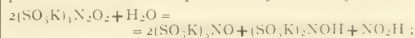


whilst Hantzsch and Semple have re-named the sulphazilate "nitroxydisulphonate" with the formula, $\text{O}:\text{N}(\text{SO}_3\text{K})_2$, and have gone back to Claus's formula for the metasulphazilate.

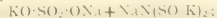
The author has found that (1) potassium sulphazilate interacts with normal potassium sulphite—



to form normal potassium hydroxylaminedisulphonate and potassium metasulphazilate; (2) the sulphazilate decomposes spontaneously into the metasulphazilate, hydroxylaminedisulphonate, and much nitrous acid, the last being preserved as nitrite when potassium hydroxide is present,—



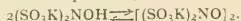
(3) potassium metasulphazilate is decomposed quantitatively into sulphate and normal aminedisulphonate (imino-sulphate) by sodium amalgam or by the zinc-copper couple, $\text{KO} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{N}(\text{SO}_3\text{K})_2 + 2\text{Na} =$



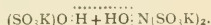
and (4) the ultimate products of its hydrolysis, when heated with hydrochloric acid, are hydroxylamine and sulphuric acid.

The molecular magnitude of sodium hydroxylaminetrisulphonate, and also of the 2-3-normal sodium hydroxylaminedisulphonate, as determined by Loewenherz's method, is in each case that which contains only one atom of nitrogen. The constitution of the sulphazilates is therefore that expressed by the name, potassium peroxylaminesulphonate, and the formula

$\text{SO}_3\text{K}_2\text{NO}\cdot\text{NO}(\text{SO}_3\text{K})_2$, and of the metaspulphazilates that expressed by the name and formula, potassium hydroxylaminetrisulphonate, $(\text{SO}_3\text{K})_2\text{N}\cdot\text{O}\cdot(\text{SO}_3\text{K})$. The sulphazilates are oxime peroxides or peroximes, being produced by oxidising hydroxylaminedisulphonates with a variety of reagents (including ozone), even in the cold; they behave as oxidising agents, becoming again reduced to hydroxylaminedisulphonates,—



A metaspulphazilate is the only known case of a triacylated hydroxylamine. Having, as a hydroxylaminetrisulphonate, one of its sulphonate radicles in union with oxygen, it is clearly one-third sulphatic, yet without being actually a sulphate. It is a mixed oxide or anhydride of two acid salts, one being the acid sulphate, and the other the 2/3 normal hydroxylaminedisulphonate,—



The inorganic mixed anhydride most closely analogous to a hydroxylaminetrisulphonate is Pelouze's salt, potassium hyponitrosulphate, $(\text{SO}_3\text{K})_2\text{O}\cdot(\text{N}_2\text{O})\text{K}$, the two salts agreeing in being stable in presence of caustic alkali, and in not yielding barium sulphate with a soluble barium salt, whilst giving rise to a sulphate with sodium amalgam or zinc. To understand this behaviour, it is only necessary to assume that the metaspulphazilate ionises into three metallic cations, and a complex trivalent anion which includes within itself the sulphate radicle. Dunstan and Goulding have shown that zinc and acid reduce trialkylhydroxylamines to trialkylamines, so that if, as has hitherto been supposed, metaspulphazilates were oxamines, they should reduce to aminetrisulphonates (nitrosulphates) and not to aminedisulphonates and sulphates. The author concludes that the nitrogen of the sulphazilates and metaspulphazilates is exclusively tri- and not quinquevalent, as suggested by the earlier investigators of these salts.

There is so much difference between the properties of a peroxylaminesulphonate and those of the bluish-violet substance produced by the action of sulphur dioxide on a solution of nitrosulphuric acid in sulphuric acid that it is improbable that Sabatier's suggestion will prove correct as to the latter compound being the acid of Fremy's bluish-violet salt.

Potassium hydroxylaminetrisulphonate is shown to have 3/2 mols. of water of crystallisation, whereas Claus, who stated that the salt contained 1 mol. of water, was perhaps unaware that some of its water of crystallisation becomes fixed by hydrolysis during the drying. Sodium, ammonium, and hydroxy-lead hydroxylaminetrisulphonates have been prepared for the first time.

*167. "Peroxylaminesulphonic Acid." By E. DIVERS.

In support of Sabatier's assumption that the bluish-violet colour caused by the action of sulphur dioxide on sulphuric acid containing nitrosulphuric acid is due to the formation of the unknown acid of Fremy's bluish-violet potassium salt (sulphazilate or peroxylaminesulphonate), it is pointed out that the difference in properties observed by Haga (preceding note) is hardly greater than that between the behaviour of nitrous acid in the respective forms of nitrosulphuric acid and potassium nitrite.

Sabatier's observations are shown to be quite consistent with the view that the acid is peroxylaminesulphonic acid; that is, a peroxide and a compound of trivalent nitrogen.

*168. "Constitution of Nitric Peroxide." By E. DIVERS.

Haga's examination of Fremy's sulphazilate has established that it is peroxylaminesulphonate, a trivalent nitrogen compound and a peroxide. It is a sulphonated nitric peroxide, as suggested by Hantzsch and Semple, and when decomposed by water, gives a complex anhydrosulphate (hydroxylaminetrisulphonate), on the one hand, and, on the other, nitrous acid and sulphonated nitrous acid (hydroxylaminedisulphonate), equivalent respectively to the nitric and nitrous acids which are yielded by nitric

peroxide. Dinitric peroxide is therefore a true peroxide, nitrosyl peroxide, $(\text{NO})_2\text{O}_2$.

Mononitric peroxide must therefore be regarded as $\text{O}\cdot\text{N}\cdot\text{O}$, formulated with a univalent oxygen atom, and not with its nitrogen atom in the quadrivalent condition, $\text{O}\cdot\text{N}\cdot\text{O}$, as suggested by Piloty and Schwerin (*Ber.*, 1901, xxxiv., 1884 and 2354). For it seems appropriate to consider the constitution of the two forms of nitric peroxide to be the same, the only difference being the presence in the one form of the bivalent double atom of oxygen, and in the other form of a single univalent oxygen atom. A true peroxide is correctly defined as a compound in which some or all of the oxygen is exerting on the rest of the compound only half its usual valency. Piloty and Schwerin's porphyrine, $(\text{C}_5\text{H}_5\text{N}_3):\text{NO}$ (*loc. cit.*) is to be regarded as being such a peroxide.

169. "Halogen Derivatives of Diphenyl and Dihydroxydiphenyl." By J. C. CAIN.

The author has already shown that only a small amount of 3:3'-dichloro-4:4'-dihydroxydiphenyl is obtained by boiling the corresponding diazonium salt with water (*Trans.*, 1903, lxxxiii., 688), and now describes a method for preparing the substance by chlorinating 4:4'-dihydroxydiphenyl.

The following compounds are described:—3:3'-Dichlorodiphenyl, white needles, m. p. 29°, b. p. 298°; 3:4:3':4'-tetrachlorodiphenyl, white needles, m. p. 172°, b. p. 230° under 50 m.m. pressure; 4:4'-dibromo-3:3'-dichlorodiphenyl, white needles, m. p. 176—177°; 4:4'-diiodo-3:3'-dichlorodiphenyl, pale yellow needles, m. p. 162°, b. p. 275° under 10 m.m. pressure; 4:4'-dicyano-3:3'-dichlorodiphenyl, white needles, m. p. 152—153°; 3:3'-dichlorodiphenyl-4:4'-dicarboxylic acid, white needles, m. p. 287—288°; 3-Chloro-4:4'-dihydroxydiphenyl, white needles, m. p. 215°. 3:3':5(2')-Trichloro-4:4'-dihydroxydiphenyl, white needles, m. p. 179°.

170. "Notes on some Natural Colouring Matters." By A. G. PERKIN and E. PHIPPS.

The flowers of the *Prunus spinosa* contain both quercetin and kampherol, whereas in the violet (*Viola odorata*) and white clover (*Trifolium repens*) quercetin alone has been detected. From the Japanese dye-stuff "Fukugi" (botanical origin unknown), a new colouring matter, $\text{C}_{17}\text{H}_{12}\text{O}_6$, has been isolated, forming yellow, prismatic needles (m. p. 288—290°), the general properties of which indicate that it is closely allied to luteolin. On bromination, it yields the compound $\text{C}_{17}\text{H}_{10}\text{O}_6\text{Br}_2$ (yellow needles, m. p. 280°), and, when fused with caustic alkali, phloroglucinol and protocatechuic acid are obtained.

Morinetetraethyl ether, $\text{C}_{15}\text{H}_{20}\text{O}_3(\text{OEt})_4$ (yellow, prismatic needles, m. p. 126—128°), closely resembles the corresponding methyl derivative and forms the colourless acetyl compound, $\text{C}_{15}\text{H}_{18}\text{O}_3(\text{OEt})_4\cdot\text{C}_2\text{H}_3\text{O}$ (needles, m. p. 121—123°). When brominated in the presence of alcohol, myricetin yields a mixture of tetrabromomyricetin and tetrabromomyricetin ethyl ether, $\text{C}_{15}\text{H}_8\text{Br}_4\text{O}_7\cdot\text{OEt}$ (colourless needles melting completely at 146°).

Cryoscopic determinations of the molecular weight of its acetyl derivative indicate that hesperitin has the formula $\text{C}_{16}\text{H}_{14}\text{O}_6$, and not $\text{C}_{32}\text{H}_{32}\text{O}_{12}$, as previously suspected by the formation of the alkali salts, $\text{C}_{32}\text{H}_{32}\text{O}_{12}\text{K}$ and $\text{C}_{32}\text{H}_{32}\text{O}_{12}\text{Na}$ (*Trans.*, 1898, xxxi., 1031). Benzoylcurcumin (yellow needles, m. p. 176—178°) in a similar manner gave results in harmony with Clamian and Silber's formula, $\text{C}_{21}\text{H}_{20}\text{O}_6$ (*Ber.*, 1897, xxx., 190), for curcumin.

171. "The Estimation of Methyl Alcohol in Presence of Ethyl Alcohol." By T. E. THORPE and J. HOLMES.

The authors described a method of estimating the amount of methyl alcohol in mixtures of methyl and ethyl alcohols based on the different modes of action of a mixture of potassium dichromate and sulphuric acid on the two alcohols. The method differs from that already described by Dupré, in 1876, in which the amount of acetic acid formed is taken as a measure of the amount of ethyl

alcohol present, in that the amount of carbon dioxide evolved is weighed.

The authors described how their method is applicable to the case of the methylated spirit of commerce, and to the detection and determination of methylated spirit in tinctures and medicinal preparations suspected to contain it.

172. "Separation and Estimation of Silver Cyanide and Silver Chloride." By R. H. A. PLIMMER.

Freshly precipitated silver cyanide, although insoluble in cold dilute nitric acid, readily dissolves in the boiling acid, evolving the theoretical quantity of hydrogen cyanide, so that the gas, when passed into silver nitrate solution, produces an amount of silver cyanide equal in weight to the sample originally employed. In this way, silver cyanide may be quantitatively separated from silver chloride. When the cyanide has been dried at 100°, the hard lumps produced offer a greater resistance to the solvent, and if the boiling is prolonged the acid, on becoming more concentrated, oxidises a small proportion of the hydrogen cyanide.

173. "Estimation of Hydroxyl Radicles." By H. HIBBERT and J. J. SUDBOROUGH.

In attempting to determine hydroxyl groups by Tschugaeff's method (*Ber.*, 1902, xxxv., 3912), the authors have not succeeded in obtaining satisfactory results, owing to the following causes:—1. Moisture gradually penetrates through the india-rubber, even although this is coated with collodion. 2. The vapour pressure of ether varies so enormously with slight alterations of temperature. 3. Grignard's magnesium methyl iodide solution slowly absorbs atmospheric oxygen.

The following method is free from the foregoing objections; dry amyl ether is used as the medium instead of ordinary ether, and the operation is carried out in an ordinary bottle provided with a double bored india-rubber stopper, so that the bottle may be attached to (1) a Lunge's nitrometer filled with dry mercury, (2) a glass tube provided with a stopcock, so that the air in the apparatus may be replaced by dry nitrogen. The amyl ether solution of the hydroxyl compound is placed in the bottle, and a solution of Grignard's magnesium methyl iodide in the same solvent is introduced in a small tube; when a constant temperature has been attained, the two solutions are mixed.

Satisfactory results have been obtained with α - and β -naphthols, resorcinol, *o*-nitrophenol, acetoxime, deoxybenzoin, and chloral hydrate.

Quinol gives somewhat low results, probably owing to the fact that it is only sparingly soluble in amyl ether.

174. "Diortho-substituted Benzoic Acids. Part V. Formation of Salts from Diortho-substituted Benzoic Acids and Organic Bases." By J. J. SUDBOROUGH and W. ROBERTS.

Since the publication of Part IV. (*Trans.*, 1899, lxxv., 580), E. Fisher has shown (*Ber.*, 1900, xxxiii., 345, 1967) that diortho-substituted tertiary bases of the type of dimethylmesidine are incapable of forming quaternary ammonium salts. The authors have prepared several mono- and diortho-substituted tertiary amines, and find that these are capable of combining with strong diortho-substituted benzoic acids, for example, 5-trinitrobenzoic and 2:4:6-tribromo-3-aminobenzoic acids, but will not unite with feeble acids like 2:4:6-trimethylbenzoic and *o*-toluic acids.

In addition to the ordinary normal salts (1 mol. acid + 1 mol. base), acid salts of the type (2 mols. acid + 1 mol. base) derived from monobasic acids and monoacidic bases have been obtained. Many of these salts can be analysed by direct titration in alcoholic solution with standard barium hydroxide solution, using phenolphthalein as the indicator.

175. "cis- π -Camphanates of *d*- and *l*-Hydrindamines." By F. S. KIPPING.

cis- π -Camphanic acid gives with *dl*-hydrindamine two

isomeric salts melting at 173° and 193° respectively, but which have the same specific rotation in aqueous solution (*Trans.*, 1900, lxxviii., 903).

Having recently succeeded in resolving the *dl*-base (*Trans.*, 1903, lxxxiii., 873), the author examined the *cis*- π -camphanates of the *d*- and of the *l*-base, partly to prove that the compounds previously described are really partially racemic, and partly to ascertain whether each of the optically active bases gives isomeric salts.

d-Hydrindamine *cis*- π -camphanate, obtained by combining the acid with the base from pure *d*-hydrindamine *d*-bromocamphorsulphonate, crystallises from water and alcohol in long needles and melts at about 181°; when fractionally crystallised from aqueous alcohol, the final mother liquors yield fractions which melt very indefinitely at 170–175°; the specific rotation of various fractions of this salt, examined in 2 per cent methyl alcoholic solution, varied from $[\alpha]_D = 7.8$ to -17.8 .

l-Hydrindamine *cis*- π -camphanate, prepared from the base contained in pure *l*-hydrindamine *d*-bromocamphorsulphonate, closely resembles the salt of the *d*-base, but the original preparation melts indefinitely at 186–191°; when crystallised fractionally from aqueous alcohol, it yields portions melting as low as 180–184°. The specific rotation of fractions of this salt, determined in 2 per cent methyl alcoholic solutions, varied from $[\alpha]_D = 6'$ to $+7'$.

These observations seem to justify the conclusion that each base gives two isomeric salts, which, when the *dl*-base is used, combine in pairs to form the two partially racemic compounds previously described. The whole of the *cis*- π -camphanic acid used in these and in previous experiments was collected and crystallised fractionally from alcohol: the first and last fractions crystallised in identical forms, namely, characteristic hexagonal plates (*Trans.*, 1896, lxi., 943), melted simultaneously, and had the same specific rotation in alcoholic solution.

176. "Resolution of *dl*-Methylhydrindamine." By G. TATTERSALL.

In resolving *dl*-methylhydrindamine into its enantiomorphously related components by the use of *d*-bromocamphorsulphonic acid (*Trans.*, 1903, lxxxiii., 918), the yield of salts of the *d*- and *l*-bases was always small, and the author, at Dr. Kipping's suggestion, attempted to find a more satisfactory process for the resolution of this *dl*-base.

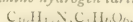
Experiments then showed that *d*-tartaric acid, used so as to form the hydrogen tartrates of the base, effected an excellent separation of the *d*- and *l*-bases by crystallising the salt at the ordinary temperature. The most sparingly soluble fractions contained the hydrogen tartrate of the *d*-base. The purification of the bases was effected by converting the first fractions, containing chiefly the *d*-base (about one third of the whole), and the last fractions separately into the *d*-bromocamphorsulphonates and finally fractionating from water.

d-Methylhydrindamine hydrogen tartrate,—



crystallises from water in long, glassy prisms; it melts at 153–155° with slight decomposition. In aqueous solution, it has a specific rotation $[\alpha]_D +33^\circ$ and molecular rotation $[M]_D = 99$.

l-Methylhydrindamine hydrogen tartrate,—



crystallises from water in aggregates of small, glassy, prisms; it melts at 197° with slight decomposition. In aqueous solution, its specific rotation is $[\alpha]_D -5^\circ$ and its molecular rotation $[M]_D -14.8^\circ$.

177. "Isomeric Salts of *d*- and *l*-Methylhydrindamines with *d*-Chlorocamphorsulphonic Acid." By G. TATTERSALL.

In a recent communication (Tattersall and Kipping, *Trans.*, 1903, lxxxiii., 918), the formation of isomeric salts by the combination of *d*- and *l*-methylhydrindamines with *d*-bromocamphorsulphonic acid has been described, and

similar experiments have now been made with the same bases and *d*-chlorocamphorsulphonic acid.

The salt of each base was made from carefully purified material and subjected to prolonged fractional crystallisation; the end fractions were then examined. In the cases of both the *d*- and *l*-bases, the melting-points of the successive fractions gradually fell from the first to the last fractions, this behaviour being also observed with the *d*-bromocamphorsulphonate.

The chlorocamphorsulphonates differ, however, from the bromocamphorsulphonates in their optical behaviour. With the former acid, the specific rotations of the last fractions are higher than those of the first fractions, whereas with the latter acid the opposite was the case. The statement is true for both aqueous and chloroform solutions.

The results obtained are summarised in the following table:

l-Methylhydrindamine *d*-chlorocamphorsulphonate.

	[α] _D
First fraction	m. p. 239° In chloroform. +33° In water. +34.2°
Last "	231–233° 8.0 35.8

d-Methylhydrindamine *d*-chlorocamphorsulphonate.

	[α] _D
First fraction	m. p. 247° In chloroform. +56° In water. +60°
Last "	225–230° 63 63

Both salts crystallise in anhydrous needles.

Similar results were obtained with hydrindamine *d*-chlorocamphorsulphonates (Kipping, *Trans.*, 1903, lxxxiii., 902), but in this case it was found impossible to isolate the isomeride of higher specific rotation.

178. "The Four Optically Isomeric *l*-Menthylamines and their Salts." By F. TUTIN and F. S. KIPPING.

The principal object of this research was to ascertain whether *l*-menthylamine would give, with *d*-bromocamphorsulphonic acid, isomeric salts analogous to those obtained by combining this acid with the optically active hydrindamines (*Trans.*, 1903, lxxxiii., 873) and methylhydrindamines (*loc. cit.*, p. 918): for this purpose, it was first necessary to obtain the *l*-menthylamine free from optical isomerides. An examination of the menthylamine prepared by reducing the oxime of "*l*-menthone" showed that the crude basic product was a mixture of four optically isomeric acid bases, and that the menthylamine obtained by heating "*l*-menthone" with ammonium formate was likewise composed of these four isomerides.

The explanation of these facts is afforded by a consideration of the optical configuration of *l*-menthone—a ketone which readily undergoes partial racemisation—and also of the reactions by means of which it is transformed into the base.

Since the four isomerides in question are derivatives of *l*-menthone (–) and of *iso-l*-menthone (+), they are distinguished as *l*-menthylamine, neo-*l*-menthylamine, *iso-l*-menthylamine (*d*-menthylamine in the literature), and *isoneo-l*-menthylamine respectively.

l-Menthylamine combines with *d*-bromocamphorsulphonic acid, giving a mixture of isomeric salts. One of these compounds can be obtained in a pure condition by repeated fractional crystallisation from water; it melts at about 226° and has a specific rotation [α]_D +43.7° in aqueous, and [α]_D +48.7° in chloroform solution. The isomeric salt cannot be obtained in a pure condition, but its presence is conclusively proved by the fact that the more readily soluble fractions melt at about 221° and have a specific rotation [α]_D +38.8° in aqueous, and [α]_D +42.8° in chloroform solution.

For the separation of the four isomeric *l*-menthylamines in the crude base, their hydrochlorides, *d*-bromocamphorsulphonates, and *d*-camphorsulphonates were fractionally crystallised, and also their formyl derivatives: *l*-menthylamine is thus isolated without difficulty, but for the separation of the other three isomerides, fractional crystallisation

of their benzoyl derivatives was found to give the best results.

The following compounds are described:—

	M. p.	[α] _D
<i>l</i> -Base	226°	+43.2°
neo- <i>l</i> -Base ..	70–75°	—
<i>iso-l</i> -Base ..	166	+65
<i>isoneo-l</i> -Base ..	—	—
<i>l</i> -Base	158	+5.3
neo- <i>l</i> -Base ..	188	+11.8
<i>iso-l</i> -Base ..	177	+21.7
<i>isoneo-l</i> -Base ..	—	—
<i>l</i> -Base	156	–61.9
neo- <i>l</i> -Base ..	128	–17.4
<i>iso-l</i> -Base ..	121	+22.7
<i>isoneo-l</i> -Base ..	104	–3.8

The specific rotations of the salts were determined in aqueous solutions, those of the benzoyl derivatives in chloroform.

179. "Preparation of the Tetra-Alkyl Derivatives of Stannimethane." By W. J. POPE and S. J. PEACHEY.

The preparation of the mixed tetra-alkylstannimethanes by the action of a zinc alkyl upon a trialkylstannimethyl iodide is difficult to carry out owing to the occurrence of secondary reactions, which greatly diminish the yield of the desired product. The authors have found that the magnesium alkyl iodides, bromides, and chlorides prepared by the method given by Grignard react vigorously with stannic chloride or with the mono-, di-, and tri-alkylstannimethane halogen derivatives, giving rise to the corresponding tetra-alkylstannimethanes. After treating the product with water, the tetra-alkyl derivative is readily separated in a state of purity by fractional distillation of the ethereal solution.

Tetraethylstannimethane, SnEt₄, is prepared by adding stannic chloride (1 mol.), dissolved in light petroleum, to the ethereal solution of magnesium ethyl bromide (4.5 mols.), washing with dilute acetic acid and distilling the ethereal solution; it boils at 180–181° under 758 m.m. pressure.

Dimethyldiethylstannimethane, SnMe₂Et₂, may be prepared either by the action of magnesium methyl iodide on diethylstannimethylene chloride, bromide, or iodide, or by that of magnesium ethyl bromide on dimethylstannimethylene chloride, bromide, or iodide in ethereal solution. After treating with water and distilling the ethereal solution, the substance is obtained as a colourless liquid identical with that prepared by Frankland's method.

Trimethylethylstannimethane, SnMe₃Et, is obtained by treating trimethylstannimethyl bromide or iodide with the calculated quantity of magnesium ethyl bromide in ethereal solution, washing with dilute acetic acid, and fractionally distilling the ethereal solution; it boils at 107–108° under 758 m.m. pressure.

Trimethylpropylstannimethane, SnMe₃Pr, is similarly prepared by the action of magnesium propyl bromide or iodide on trimethylstannimethyl bromide and forms a colourless liquid boiling at 120° under 764 m.m. pressure.

Triethylpropylstannimethane, SnEt₃Pr, from triethylstannimethyl bromide, boils at 195° under 764 m.m. pressure.

Dimethylethylpropylstannimethane, SnMeEtPr, prepared by the action of propyl magnesium bromide or iodide on dimethylethylstannimethyl bromide, boils at 153° under 762 m.m. pressure.

Methylethyldipropylstannimethane, SnMeEtPr₂, obtained from methylethylstannimethylene iodide and magnesium propyl bromide, is a colourless liquid boiling at 183–184° under 758 m.m. pressure.

Tetraphenylstannimethane, SnPh₄, is conveniently prepared by the action of stannic chloride on magnesium phenyl bromide.

The further study of the mixed alkylstannimethanes, prepared by aid of the above reaction, is being continued, together with the examination of the action of the magnesium alkyl salts on silicon tetrachloride.

180. "Optically Active Esters of β -Ketonic and β -Aldehydic Acids. Part IV. Condensation of Aldehydes with Menthyl Acetoacetate." By A. C. O. HANN and A. LAPWORTH.

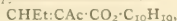
Menthyl acetoacetate condenses readily with aldehydes in presence of bases, and the following products have been obtained.

Dimenthyl ethylidenebisacetoacetate.—



produced when acetaldehyde is used, forms fine needles melting at $194-196^\circ$ and has $[\alpha]_D -24.9^\circ$ in benzene, a very slight mutarotation being noticed.

Menthyl n-propylidenebisacetoacetate.—



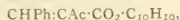
is formed at the ordinary temperature, crystallises in glistening, elongated plates or needles, melts at $84-88^\circ$, and has $[\alpha]_D -34.9^\circ$. It condenses with menthyl acetoacetate to form *dimenthyl n-propylidenebisacetoacetate*, $\text{CHET}(\text{CHAc} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19})_2$, which melts at $201-207^\circ$ and has $[\alpha]_D -26.9^\circ$.

Dimenthyl n-butylidenebisacetoacetate.—



melts at about 184° and has $[\alpha]_D -16.8^\circ$. *Dimenthyl isobutylidenebisacetoacetate*, $\text{CHPr}(\text{CHAc} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19})_2$, melts at $193-202^\circ$; in benzene solution, it has $[\alpha]_D -42.6^\circ$, changing slowly to $[\alpha]_D -46.0^\circ$.

Menthyl benzylidenebisacetoacetate.—



crystallises in well-formed, glistening plates melting at $133-134^\circ$ in benzene solution, $[\alpha]_D -10.0^\circ$. With menthyl acetoacetate, it yields *menthyl benzylidenebisacetoacetate*, $\text{CHPh}(\text{CHAc} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19})_2$, which melts at $203-206^\circ$ and has $[\alpha]_D -30.4^\circ$.

The formula usually ascribed to the monoalkylidene derivatives of β -ketonic esters does not readily account for the abnormally low values of their rotatory powers.

The statement that tertiary bases are not effective in bringing about the condensation of aldehydes with β -ketonic esters is incorrect; the very feeble tertiary bases, pyridine, quinoline, or dimethylaniline, are useless, but trimethylamine and tripropylamine may be employed, although these are not so rapid in their action as the still more powerful secondary bases, such as diethylamine or piperidine.

181. "Estimation of the Adulterant in Citronella Oil." By M. K. BAWLER.

A mixture of 2 c.c. of pure cocoanut oil free from acid



and 2 c.c. of the citronella oil under examination is shaken for one minute with 20 c.c. of 83 per cent of alcohol (sp. gr.

0.8273 at 30°) in the graduated tube (see Fig.), this vessel being then rotated in a centrifugal machine for 0.5 to 1 minute. The volume of cocoanut oil, which now contains the impurity originally present in the citronella oil, is ascertained, and this reading minus 2 c.c. represents the adulterant. For example, 2.45 c.c. of residual oil represent 0.45 c.c. of impurity in the 2 c.c. of citronella oil or an adulteration of 22.5 per cent. A standard oil should be tested occasionally against the unknown samples in order to eliminate errors arising from the use of alcohol of different strengths.

In this way, the adulterant is separated and estimated in three or four minutes, the test being conducted at $20-30^\circ$.

NOTICES OF BOOKS

Elementary Practical Chemistry. Part I., General Chemistry. Part II., Analytical Chemistry, Qualitative and Quantitative. By FRANK CLOWES, D.Sc. (Lond.), and J. B. COLEMAN, A.R.C.Sc. Fourth Edition. London: J. and A. Churchill. 1903. Pp. 211 and 198.

THE present edition has been published in two parts. Part I. has been arranged to suit the requirements of the general science student, and it is hoped that it will be found convenient to students of this class; students of pure and applied chemistry who require careful training in analytical methods will find a complete course of qualitative analysis, including a few examples of quantitative methods in Part II. Most students will require both parts if they really intend to make a serious study of chemistry, and if their chemical future is not bounded by the inevitable exam.; still, we are of the opinion that this division of the book is a wise one, as the two volumes separately are more handy in form than the one larger one.

It is a pity, however, that the two volumes have not been better matched; the paper used for Part II. is quite different to that used in Part I., and even the lettering on the backs is not in the same style.

Part I. commences with a description of the metric system, and gradually lays the principles of chemistry before the student by means of a selected series of experiments. Many quantitative experiments are given, and this part concludes with a selection of examples to test the progress of the student.

Part II. begins with descriptions of various ordinary chemical operations, such as ignition, precipitation, and filtration. Then follow descriptions of the reactions and methods of detection of the common metals and acids.

Quantitative analysis, both gravimetric and volumetric, is next in order; the volumetric methods described include acidimetry and alkalimetry, and estimations by means of oxidation, reduction, and precipitation. The gravimetric estimations are the well-known ones, and are combined with the usual group reagents for the separation of the metals.

The general arrangement of these two volumes is good, as is also the printing, while each volume is provided with an adequate table of contents and an index.

Year-Book of Pharmacy. Edited by J. O. BRAITHWAITE. London: J. and A. Churchill. 1903. Pp. 659.

THIS volume comprises abstracts of papers relating to materia medica, pharmacy, and chemistry, contributed to British and foreign journals from July 1st, 1902, to June 30th, 1903, with the Transactions of the British Pharmaceutical Conference at the fortieth annual meeting, held in Bristol, July, 1903. The compilation of such a volume is by no means a light undertaking, and the editors are to be congratulated on the satisfactory result of their labours, which will no doubt be of service to all pharmaceutical chemists.

Annual for the Year 1904. ("Annuaire pour l'An 1904"). Published by the Bureau des Longitudes. Paris: Gautier-Villars. Pp. 732.

Certain new arrangements are here inaugurated in the compilation of this annual. For instance, detailed tables are given relative to physical and chemical science, while the geographical and statistical tables have been omitted.

In the astronomical portion, the data relative to calendars, and more especially ancient calendars, have received more attention, and a complete table of the elements of the small planets has been inserted. Among the matters that have been omitted are the calculation of altitudes from the height of the barometer, stellar parallaxes, double stars, &c.

The physical portion contains many additions, such as the magnetic elements at various points on the earth's surface; the dilatation of various liquids; the vapour tension of various liquids, mercury in particular; a table of wave lengths, by M. de Gramont; the solubility of various substances in water, &c., and the chemical portion has been completed by the addition of a table of the principal alloys.

Dictionary of Hygiene. B. C. T. KINGZETT, F.I.C., and D. HOMFRAY, B.Sc. Second Edition. London: Ballière, Tindall, and Cox, 1904. Pp. 112.

In these pages the authors have given concise information respecting most of the subjects comprehended in the theory and practice of hygiene, so far as they can be dealt with in pocket-book form. In this edition several fresh articles have been introduced, and some of the subjects dealt with in the previous edition have been treated more fully. The book is handy in form, and as it measures only 3 x 5 inches, it will easily go in the pocket, where it is always ready for reference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

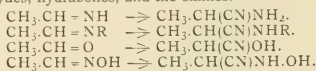
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxvii., No. 23, December 7, 1903.

A New Method of Calculating Heats of Combustion.—P. Lemoult.—In a previous communication the author showed that the heat of combustion of carbides and their oxygen derivatives can be calculated from that of the elementary groups ($C_3 \equiv C_3$), $-(C_2 - C_2)$, . . . $(C - H)$ and of the functional groups. This method led him to apply two series of formulae to extend his research:—(1) $C_4 - 157n + A_1$; (2) $C_2 - 463m + A_2 \equiv 115.75n + A_2$. The first for acyclic compounds, the second for cyclic compounds (n being the number of atoms of C, m the number of the order of the generating cyclic carbide).

Researches on Azoic Compounds, New Method of Formation of Indazylic Derivatives.—P. Freundler.—Investigations on azoic compounds possessing an alcoholic or ortho-substituted ether oxide function show the facility with which the indazylic radicle is produced; *o*-azobenzonic and *o*-hydrazobenzonic acetals furnish a very striking example. The transformation of these compounds into indazols can be effected at a comparatively low temperature, and under the influence of agents which are not very energetic. Further, this implies a previous modification of the functional groups which cannot usually be effected during the conditions under which the author works.

Action of Hydrocyanic Acid on Ammonium Aldehyde and Analogous Combinations.—Marcel Delépine.—The action of hydrocyanic acid on the am-

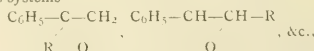
monium aldehydides constitutes one of the methods of synthesis of the α -amino acids. The transformations may be represented generally by various equations according to different experimenters, and the author now shows that the classic equations which show the elements of water intervening and expressing a theoretical yield of aminonitrite ought to be modified. The most simple modification is first to assume that the hydrocyanic acid fixes itself on to the double liaisons of the imines as is the case with the aldehydes, hydrazones, and the oximes.



New Action of Hydroxylamine.—L. J. Simon.—When a few drops of a very dilute solution of sodium nitroprussiate and a small excess of soda or potash are added to a dilute solution of a salt of hydroxylamine, and the liquid is gradually raised to boiling-point, it changes its colour from yellow, first to an orange-red, and finally takes a beautiful cerise red colour. During this process nitrogen and nitrous oxide gas are evolved. This reaction can often be used with great advantage for the identification of hydroxylamine.

New Method of Preparation of Aldehydes.—L. Bouveault.

Phenyl Migration.—Marc Tiffeneau.—The author makes a series of experiments on phenylic migration, and comes to the conclusion that in the passage from the unstable form of ethylene oxide to the corresponding stable form, aldehyde or ketone, the phenyl radicle is more mobile than the hydrogen, and this in its turn more mobile than the alkyl radicle (ethyl, amyl, or benzyl). In the various systems—



it is always the phenyl which migrates, whilst in the corresponding systems where the C_6H_5 is replaced by an alcoholic radicle, it is always the hydrogen and not the alkyl which migrates. Finally, in systems such as—



showing no free hydrogen atom, it is the phenyl which tends to migrate.

Ethers of Isopropylmucic Acid.—G. Chavanne.—Methylic and ethylic ethers of isopropylmucic acid can not be obtained by any of the usual methods. The author succeeds, however, in isolating them by the use of dimethylic and diethylic sulphates. Their stability towards water and dilute acids places them rather amongst the ethers of phenols than amongst the ether salts.

Ethylic Alcohol Hydrates.—E. Varenne and L. Godefroy.—The hydrate of alcohol, $C_2H_5.OH + 3H_2O$, has been known for some time. This corresponds to 52.3 vols. of alcohol mixed with 47.7 vols. of water at 15°, and gives the maximum of contraction. In order to investigate various mixtures and compounds of alcohol and water the authors use a special apparatus called a chrono-stroscope, of which they describes the construction and use.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 10.

This number contains no chemical matter that has not been already noticed in our columns.

NO. II.

Application of the Law of Phases to the Examination of the Distillation of Pine-resin.—M. Vêzes.—A long paper not suitable for abstraction.

Elimination and Distribution in the Organism of Medicinal Arsenic in the Form of Methyl Arsenate of Soda.—A. Mouneyrat.—The author shows that whatever the dose of methyl arsenate of soda absorbed, there is a maximum elimination in the first four or five hours after the absorption; then from this moment, its excretion, for

the same lapse of time, diminishes progressively. After twenty-four hours, about three-fifths of the substance is eliminated, but the whole is not eliminated until the thirty-second day.

Influence of the Chemical Form under which an Element is Presented to the Organism, on the Rapidity of its Passage into the Blood.—A. Mouneyrat.—As a result of experiments made with arsenic on dogs, the author finds that the blood of dogs that received the arsenic in the mineral form (arsenate and arsenite), contained more arsenic than that of dogs that received the same metalloid in the organic form.

The Solubility of Hard Copals.—Ch. Coffignier.—Experiments show that Zanzibar copal is more insoluble than that from Madagascar, no matter what solvents were used. The solvents tried were ethylic, methylic, and amylc alcohols, sulphuric ether, chloroform, acetone, benzene, aniline, acetate of amyl, and others. The actual results are all given in tabular form.

MISCELLANEOUS.

South - Western Polytechnic, Chelsea.—The Governing Body of this Institute have accepted with very great regret the resignation of the Principal, Mr. Herbert Tomlinson, F.R.S. At their meeting held December 16th, 1903, the following resolution was passed:—"That the Governing Body hereby desire to record their cordial appreciation of the admirable work that Mr. Tomlinson, as the first Principal, has accomplished in organising and developing the Institute in all its branches."

Royal Institution.—On Tuesday next, January 12, at 5 o'clock, Prof. L. C. Miall will commence a course of six lectures at the Royal Institution on "The Development and Transformations of Animals"; on Thursday, January 14, at the same hour, Mr. G. R. M. Murray delivers the first of three lectures on "The Flora of the Ocean"; and on Saturday, January 16, at 3 o'clock, Mr. J. A. Fuller Maitland begins a course of three lectures on "British Folk Song" (with Vocal Illustration). The Friday Evening Discourse on January 15 will be delivered by the Rt. Hon. Lord Rayleigh, his subject being "Shadows"; on January 22 by the Rev. W. Sidgreaves on "Spectroscopic Studies of Astrophysical Problems at Stonyhurst College Observatory"; and on January 29 by Mr. D. G. Hogarth on "The Marshes of the Nile Delta."

Iodometric Estimation of Thallium by Precipitation in the Form of Chromate.—E. Rupp.—The volumetric estimation of thallium proposed by Messrs. Browning and Hutchins gives only approximate figures (*Am. Chem. Soc.*, vol. i., p. 35). The difficulty consists in the easy solubility of the chromate of thallium in water (100 parts of water dissolves 0.03 grm. of the salt at 60°). However, we can obtain exact results by proceeding as with bismuth. The following is the method recommended by Rupp for making the estimation:—Take 10 or 20 c.c. of a 5 per cent solution of chromate of potassium, in which the proportion of CrO_3 is known exactly, and place them in a 50 or 100 c.c. beaker, with an equal quantity of water, and 1 or 2 grms. of carbonate of lime. To this solution we add the solution of the salt of thallium, which should be neutral, and should not contain more than 0.1 grm. of thallium. We then make the liquid up to a known volume, leave it to stand for thirty minutes, throw on a filter, and estimate the excess of CrO_3 on an aliquot part of the filtrate (about 20 to 50 c.c.). To effect this, dilute to 100 c.c., add 10 or 15 c.c. of 25 per cent hydrochloric acid, then 1 grm. of iodide of potassium; let stand for five minutes, and titrate with hyposulphite. By making the same estimation on the original chromate solution, we obtain, by difference, the chromic acid utilised for the precipitation of the thallium. The number of c.c. of decinormal hyposulphite corresponding to this chromic acid, $\times 0.01362$, gives the amount of thallium.—*Zeit. Anorg. Chem.*, vol. xxxiii., p. 156.

MEETINGS FOR THE WEEK.

TUESDAY, 12th.—Royal Institution, 5. "Development and Transformations of Animals," by Prof. L. C. Miall, F.R.S.
WEDNESDAY, 13th.—Society of Arts, 8 (Juvenile Lectures). "Navigation of the Air," by Eric Stuart Bruce, M.A.
THURSDAY, 14th.—Society of Arts, 4.30. "The Presidency of Bombay," by Sir William Lee-Warner, K.C.S.I.
—Royal Institution, 5. "The Flora of the Ocean," by G. R. M. Murray, F.R.S.
FRIDAY, 15th.—Royal Institution, 9. "Shadows," by The Rt. Hon. Lord Rayleigh, O.M., F.R.S. &c.
SATURDAY, 16th.—Royal Institution, 3. "British Folk Song" (with Vocal Illustrations), by J. A. Fuller Maitland, M.A.

THE SIR JOHN GASS TECHNICAL INSTITUTE, JEWRY STREET, ALDGATE, E.C.

Principal—CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.

EVENING CLASSES IN CHEMISTRY, METALLURGY, PHYSICS, and MATHEMATICS.

Designed to meet the requirements of those engaged in CHEMICAL, METALLURGICAL, and ELECTRICAL INDUSTRIES, and in trades associated therewith.

Every facility for Special and Advanced Practical Work in well-equipped Laboratories.

CHEMISTRY		{ CHARLES A. KOHN, M.Sc., Ph.D., F.I.C., and G. SENTER, B.Sc., Ph.D.
PHYSICS		R. S. WILLOWS, D.Sc., B.A.
METALLURGY		C. O. BANNISTER, Assoc.R.S.M.
MATHEMATICS		G. W. C. KAYE, B.Sc.

CLASSES IN METALLURGY.

GENERAL METALLURGY.
THE METALLURGY OF GOLD and SILVER.
METALLOGRAPHY, including PYROMETRIC WORK.
ASSAYING.

ANALYTICAL CHEMISTRY.

Including ELECTROLYTIC and GAS ANALYSIS.

Each Course of Lectures will be accompanied by suitable Laboratory Work.

GLASS BLOWING.

Two Courses of Instruction will be given during the Lent Term by Mr. A. C. COSSOR.

New TERM begins MONDAY, JANUARY 4th, 1904.

The Institute is readily accessible, and near to Fenchurch Street, Liverpool Street, Broad Street, and Metropolitan Railway Stations.

For details of the Classes apply at the Office of the Institute, or by letter to the PRINCIPAL.

W. H. DAVISON, M.A.,
Clerk to the Governing Body.

THE CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

Five lines in column (about 10 words to line)	£ s. d.
Each additional line	0 3 6
Whole column	1 15 0
Whole page	3 0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and Coun Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2303.

ON THE GASEOUS CARBON MONOSULPHIDE DESCRIBED BY THOMSEN.

By NORMAN SMITH, M.Sc.,
Demonstrator in Chemistry, The Owens College, Manchester.

WITHIN recent years a number of attempts have been made to prepare carbon monosulphide. In 1895 Deninger (*Journ. Pr. Chem.* [2], li., 346) stated that he had obtained it by the action of sodium on a mixture of carbon disulphide and aniline, but it was shown by Russell and the author (*Journ. Chem. Soc.*, 1902, lxxxi., 1528) that the gases produced were invariably mixtures of already known substances. Last year, Julius Thomsen (*Zeit. f. Anorgan. Chem.*, 1903, xxxiv., 187), by passing a mixture of carbon disulphide and nitrogen over copper heated to dull redness, observed an increase in volume and obtained a gas which, as only nitrogen carbon disulphide and copper were originally present, he concluded was probably carbon monosulphide. On treatment with aqueous potash a small part of the gas was absorbed, due he considered to a small amount of carbon disulphide left in the gas. The residue on sparking with oxygen over aqueous potash, consumed an amount of oxygen approximately corresponding to the amount required by a substance with the formula CS. The small difference between the quantity actually used and the theoretical amount was explained by the formation of some sulphur trioxide.

Since the publication of Thomsen's paper, I have been engaged in repeating the experiments, and in carrying out a large number of somewhat tedious analyses to determine if carbon monosulphide is formed by the above method. I find that the results obtained by Thomsen can be entirely explained without assuming the formation of carbon monosulphide, for during the reaction there are invariably formed oxides of carbon, a mixture of which with carbon disulphide would give the same analytical results as were obtained by him.

Stock and K  chler (*Ber.*, 1903, xxxvi., 4336) have published a paper on the same subject since my experiments were performed. They have repeated Thomsen's experiments and tried to isolate the gas CS by condensation with liquid air, but could not obtain any evidence of a sulphur gas besides carbon disulphide. Further, they have shown that some carbon dioxide is always present, due to the fact that the copper cannot be got perfectly free from oxide.

As the question of the formation of carbon monosulphide has been thrown in doubt by these investigators, I thought it would be of interest to communicate my results, thus independently confirming the conclusions arrived at by Stock and K  chler. I do not, however, consider it necessary under the circumstances to give details of the many analyses performed.

Experimental.

At first Thomsen's experiments were repeated in the manner described by him, and the gas obtained treated with aqueous potash. The rapid absorption of a portion of the gas which took place was undoubtedly due to carbon dioxide, for carbon disulphide is only very slowly removed by aqueous potash. The residual gas was then exploded with excess of oxygen, and the sulphur dioxide and carbon dioxide produced, as well as the resulting contraction and amount of oxygen used, were determined. From these data one can calculate the amount of sulphur trioxide which is always formed in the explosion (see Russell, *Journ. Chem. Soc.*, 1900, lxxvii., 352). Varying

results were obtained with different samples of gas. In some the volumes of carbon dioxide and sulphur dioxide respectively were approximately equal, indicating a composition CS, but in other experiments, and particularly after the gas had been previously cooled in order to condense most of the carbon disulphide, the volume of carbon dioxide was larger than that of the sulphur dioxide. This led one to suspect the presence of carbon monoxide, which was further indicated by the fact that a part of the original gas was absorbed by acid cuprous chloride. Samples of the gas were then prepared and treated first with alcoholic potash to absorb carbon disulphide and carbon dioxide, and then the residual gas exploded with oxygen. Only a slight trace of sulphur dioxide could be detected, but there was a considerable quantity of carbon dioxide present. Undoubtedly, therefore, carbon monoxide was present in the gas.

Experiments were also tried without nitrogen: the whole apparatus was swept out by a current of carbon disulphide vapour obtained by boiling the liquid under reduced pressure, and the copper then heated in the stream of carbon disulphide vapour. The resulting gas was again found to contain some carbon dioxide and carbon monoxide.

In some experiments the copper was reduced by alcohol as mentioned by Thomsen, whilst in others it was heated strongly for some time in a current of hydrogen.

Manchester, January 6th, 1904.

NOTE ON THE CONNECTION BETWEEN NEGATIVE ELECTRICITY AND THE VALENCE OF ATOMS.

By GEOFFREY MARTIN, B.Sc.(Lond.).

IN the CHEMICAL NEWS last April (1903, lxxxvii., 162), I suggested that it was the negative electricity which an atom contained that determined the degree of valence with which an element can act.

That the addition of electricity to an element can often cause it to temporarily assume degrees of valence otherwise unattainable under ordinary conditions is well known.

For example, a silent electric discharge through a mixture of NO and O cooled to a low temperature causes the formation of NO₃—the N atom here acting with a valence of six—a valence which it seems incapable of assuming in any other compound.

SO₂ and O under similar conditions unite to form S₂O₇—S here acting as S^{VI}, also an otherwise unknown grade of valence.

The precise connection between the electric field in which an element is placed and the degree of valence with which the element acts seems to be indicated by the following facts:—

"When a solution of sulphuretted hydrogen in water is decomposed by an electric current, the sulphur is deposited on the positive pole, and has therefore an electro-negative nature, and this sulphur is soluble in CS₂. When a solution of sulphurous acid is decomposed in the same manner, the sulphur is deposited on the negative pole, and is therefore electro-positive; and the sulphur so deposited is insoluble in CS₂. The sulphur which is combined with metals must have the properties of the sulphur contained in sulphuretted hydrogen, whilst the sulphur combined with chlorine is like that which is combined with oxygen in sulphurous anhydride.

"Hence Berthelot recognises the presence of soluble sulphur in metallic sulphides, and of the insoluble modification of amorphous sulphur in sulphur chloride.

"Cloeze showed that the sulphur precipitated from solutions is either soluble or insoluble, according to whether it separates from an alkaline or acid solution" (Mendeleeff, "Principles of Chemistry," 1897, ii., 207).

It appears, therefore, that the divalent S in H_2S (and in metallic sulphides generally) is deposited on the anode, and therefore comes from the cathode. Whereas the polyvalent S in H_2SO_3 (and in combinations of S with non-metals generally) is deposited on the kathode, and therefore comes from the anode.

Metals behave in the same way. For example, Hittorf ("Über das Verhalten des Chroms," *Zeit. für Elektrochemie*, 1899, No. 1) shows that when metallic Cr is made the cathode it is in a divalent state, since it dissolves as CrX_2 ; whereas when anode it is hexavalent, since it dissolves as CrO_3 . Iron shows a similar behaviour.

It appears, therefore, that an element, whether metallic or non-metallic in nature, develops a high valence when made anode (*i.e.*, to receive negative electricity), and a low valence when made cathode (*i.e.*, when negative electricity is drained away from it).

This strongly supports the view that the valency of an element is connected in the way previously indicated with the quantity of negative electricity it contains.

Kiel, December 7, 1903.

PRECIPITATION OF SOME ALKALOIDS BY NITRATE OF URANIUM; REACTION OF MORPHINE.

By J. ALOY.

THE use of general reagents, such as chloride of platinum or gold, iodised potassic iodide, double iodides of potassium and mercury, or of potassium and bismuth, phosphotungstic acid, &c., for the detection of alkaloids, offers serious difficulties in many cases.

Occasionally these reagents precipitate foreign bodies, ammoniacal salts, or albumin; also the precipitates formed are often badly adapted for the recovery of the alkaloid.

I was anxious to know whether a certain number of vegetable bases could not be identified by making use of their alkaline function. I decided on using nitrate of uranium, $(\text{NO}_3)_2\text{UO}_2 \cdot 6\text{H}_2\text{O}$, as the reagent. The principal reasons I had for making this choice are as follows:—In the presence of free ammonia, uranium gives a precipitate consisting of an insoluble uranate which by simple calcination is transformed into the oxide, U_3O_8 . The weight of the oxide enables us to know immediately the amount of the base present in the compound.

Further, nitrate of uranium in dilute solution is without action on the salts and on organic matters. Finally, this salt is very soluble in alcohol, ether, and the reagents in general use for the extraction of the alkaloids.

Most of the alkaloids in etherial or aqueous alcoholic solution act on nitrate of uranium in the same manner as ammonia.

I have examined the following ones, which all give a precipitate of the uranate:—Pyridine, narcotine, papaverine, codeine, thebain, narcen, quinine, cinchonine, cinchonidine, strychnine, brucine, cocaine, pelletierine, aconitine, atropine, and cicutine.

Cafein, theobromine, and asparagine are not precipitated; as for morphine it gives a characteristic coloured reaction.

To effect the precipitation of the alkaloids, it is best to take a solution of the nitrate diluted to 5 per cent, and neutralised very carefully with ammonia until precipitation just begins. The nitrate is then added drop by drop to the solution of the alkaloid so long as the precipitate is formed.

The sensitiveness of this method is fairly great when the alkaloid is present in a small amount of the solvent. We are able to detect a tenth of a m.grm. of most of the alkaloids that I have examined. The precipitate once formed remains easily distinguishable when the solution is diluted.

If the solution under examination is very dilute, a cloudiness is produced which is transformed slowly into a precipitate.

This transformation is facilitated by keeping the temperature up to 60° or 70° .

The uranates of the alkaloids have the general properties of the alkaline uranates. They are insoluble in water and alcohol inversely as most of the salts of the alkaloids are.

Though amorphous at the moment of their formation, several of these precipitates take a crystalline form after a little time. They all have a more or less accentuated yellow colour.

I have analysed the compounds of uranic acid with pyridine, strychnine, brucine, and codeine by estimating the uranium as oxide, U_3O_8 , and the amount of alkaloid from the volume of nitrogen measured by Dumas's method. None of these compounds corresponds to the normal acid, $\text{UO}_3 \cdot \text{H}_2\text{O}$; they consist of biuranates with the general formula $\text{U}_2\text{O}_8\text{H}_2 \cdot 2\text{Alk} + \text{Aq}$. In every case analysis shows a deficit of nitrogen which is increased by washing.

The uranates enable us to recover the original alkaloids very easily. It suffices to treat them with an alkaline bicarbonate, which sets the alkaloid at liberty and dissolves the uranic acid. The alkaline uranates are also dissolved under the same conditions.

Reaction of Morphine.—Morphine and its salts in the presence of dilute nitrate of uranium give a beautiful red colouration. This reaction is due to a reduction of the uranium salt by the phenolic function of this base. It is not produced by any of the other alkaloids I have mentioned. Thus it enables us to identify morphine in a mixture.

The colouration is distinctly red with quantities of morphine greater than 5 m.grms.; it changes to an orange tint when the proportion of alkaloid diminishes.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 12.

THE USE OF BINOXIDE OF LEAD IN ANALYSIS.

By M. St. BOGDAN.

My bibliographical research, in so far as concerns the reactions which take place between bin oxide of lead and sulphuretted hydrogen in aqueous solution, and between bin oxide of lead and solutions of different metallic sulphides, has been unsuccessful.

The experiments undertaken with a view to deciding this question will be published later on.

In the meantime, I propose describing the experiments made with the object of effecting the rapid elimination of sulphuretted hydrogen or metallic sulphides from any solution.

I have observed that an aqueous solution of sulphuretted hydrogen is decomposed by powdered bin oxide of lead in the cold, with the formation of sulphide of lead. I made use of this reaction to free an alcoholic solution from traces of sulphuretted hydrogen, which was present as an impurity. After having digested the solution for three hours with bin oxide of lead in excess, there was no longer any perceptible odour of sulphuretted hydrogen. The reaction is still more rapid with the metallic sulphides, and especially so with sulphide of ammonium; and in these cases it is always accompanied with a considerable evolution of heat. M. Vraciu was kind enough to inform me of an observation made by him, that a mixture of a concentrated solution of sulphide of ammonium and powdered bin oxide of lead ignites spontaneously when an excess of the bin oxide is thrown suddenly into the solution of the sulphide.

On the above facts briefly related is founded the method I propose for the decomposition of the sulphide of ammonium that is present in excess in the solution, after the precipitation in the form of sulphides of metals, of which the salts are not precipitable by sulphuretted hydrogen in acid solution.

The great disadvantage of the method employed up to

the present for removing the excess of sulphide of ammonium after the precipitation of the said metals—decomposition of the sulphide by hot hydrochloric acid—rests in the slowness of the operation; in fact, it is necessary to heat for a long time to eliminate the sulphuretted hydrogen completely, and the filtration, which is always indispensable, is rarely very rapid on account of the sulphur which is deposited in a very finely divided state. There is also a considerable increase in volume, which necessitates the concentration of the liquid on the water-bath before searching for the bases of the following groups. On the other hand, by adding powdered biniodide of lead to the solution containing the sulphide of ammonium, my experiments have shown that this substance transforms even the last traces of the sulphide of ammonium into ammonia with the precipitation of the sulphide of lead. The reaction goes on in the cold, though it is preferable to heat for a few minutes on the water-bath.

Two series of experiments that I am about to summarise show still better the advantages of this method.

In the first series of experiments I took 10 c.c. of a saturated solution of freshly prepared sulphide of ammonium, and after having diluted up to 100 c.c., I heated this solution for five minutes with biniodide of lead in excess. After cooling the solution, I filtered it. The resulting liquid was perfectly colourless; it did not give off any odour of sulphide of ammonium, and it was not possible to detect any trace of sulphur by any reaction whatever. On evaporating a small quantity of the liquid to dryness in a platinum crucible, I found that it did not leave any residue; on the other hand, the solution contained ammonia.

The blackish-brown residue is a mixture of sulphide of lead, biniodide of lead, and sulphur.

The reaction which takes place may be expressed by the following equation:—



The importance of these experiments rests in the fact that all traces of sulphide of ammonium are destroyed, and there remains ammonia in solution as the product of the reaction.

The second series of experiments was undertaken to prove that the bases of the following groups are not carried down by this precipitation. To 50 c.c. of a normal solution of chloride of barium, I added 10 c.c. of a concentrated solution of sulphide of ammonium, and after precipitation with the biniodide of lead while heating, I filtered. The filtrate comprised the washings of the residue, and after acidulation with hydrochloric acid it was precipitated with sulphuric acid.

The quantity of sulphate of barium found showed that the whole of the chloride of barium was present in solution after the precipitation with biniodide of lead.

This operation was repeated several times on solutions containing a mixture of chlorides or nitrates of calcium, barium, and strontium; the solution, after similar treatment, always contained the same quantity of salts in solution.

It results from these experiments that on decomposing sulphide of ammonium in this manner, we can get rid of the whole of the sulphur, and that the ammonia, which is even necessary for the subsequent treatment of the substance under analysis, remains in solution.

Further, the alkaline-earth bases are not carried down by the insoluble residue, and the filtrate does not contain a trace of lead.

The simplicity of the operation, as well as the rapidity with which it can be carried out, makes it very useful. It may be also observed that this method is both more economical and more hygienic on account of there being no disengagement of sulphuretted hydrogen.

* The reaction, which I am still examining, seems to be in reality more complicated. In fact, I have found in the residue a colourless crystalline product, insoluble in ammonia, but soluble in nitric acid. It contains lead.

Being persuaded that this method, both simple and convenient, will be of great service to analytical chemists, I think I am right in not longer deferring its publication.

Before long I shall give the results of other researches now in progress on a method for the volumetric estimation of sulphuretted hydrogen and of sulphides, by the use of biniodide of lead.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 12.

BEHAVIOUR OF PHENOLPHTHALEIN IN THE PRESENCE OF BICARBONATES AND OF ALKALINE CARBONATES.

By M. GIRAUD.

PHENOLPHTHALEIN becomes pink in the presence of alkaline carbonates; I have endeavoured to find out up to what point this colouration persists when titrating these salts with sulphuric acid. Now, I have found that with a solution of CO_3Na_2 , titrating, for 10 c.c., 10.7 c.c. of molecular sulphuric acid in the presence of tropeolein, I only obtained 5.35 c.c. in the presence of phenolphthalein. Another experiment made with 53 grms. of chemically pure anhydrous CO_3Na_2 , titrated 50 c.c. with molecular acid in the presence of tropeolein, I only obtained 25 c.c. with phenolphthalein.

Through a solution of carbonate of soda red to phthalein, I passed a current of CO_2 , previously washed, and after a certain time the solution lost its colour; I made the same experiment with bicarbonate of soda containing traces of carbonate, and the decoloration was complete after a few minutes; this shows that phenolphthalein becomes pink in the presence of alkaline carbonates, and loses its colour in the presence of the corresponding bicarbonates.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 12.

THE BEHAVIOUR OF CERUM, LANTHANUM, NEODYMIUM, PRASEODYMIUM, THORIUM, AND ZIRCONIUM TOWARD ORGANIC BASES.*

By BURT LAWS HARTWELL.

(Concluded from p. 16).

p-Toluidine.—From observations made in the qualitative way, it appeared not improbable that *p*-toluidine might be employed to separate zirconium and thorium from lanthanum, neodymium, and praseodymium. Accordingly, determinations were made in about 100 c.c. of the weak alcoholic solutions, a moderate heat being applied to hasten the reaction. The precipitates formed were quite voluminous and somewhat gelatinous, especially in the case of zirconium, and well adapted for bringing down the accompanying element. On this account one re-precipitation was carried out in each case. The first precipitates dissolved readily in dilute nitric acid, especially if the solutions in the case of zirconium were not allowed to become too warm. The accompanying element was precipitated by ammonia from the combined filtrates. The ignition of the precipitates was conducted with free access of air, in a porcelain crucible usually, and the blast-lamp used till constant weights were obtained. All of the weights, recorded in grms., are given in the condensed form below. The weights given as "required" were obtained by direct precipitation of the elements, separately, and blasting to constant weight, and represent the average of two closely agreeing results. The "combined" oxides represent the sum of the individual oxides. The results obtained in many cases do not agree well with the standard, but it was thought best to include all which, so far as known, were carried through without accident. Some minor differences

* Contributions from the John Harrison Laboratory of Chemistry (From author's thesis for Ph.D. degree. Taken from the *Annals of the American Chemical Society*, N.Y., No. 14).

in manipulation, such as varying the strength of alcohol, time of digestion, temperature, and volume of solution, were made in different cases. These variations may have influenced the results in some instances.

Zirconium and Lanthanum.

Zirconium oxide—		Lanthanum oxide—		Combined oxides—	
Found	Required	Found	Required	Found	Required
0°1342	0°1341	0°0399	0°0409	0°1741	0°1750
0°1301	0°1341	0°0993	0°1023	0°2294	0°2364
0°1314	0°1341	0°1025	0°1023	0°2339	0°2364
0°1367	0°1341	0°0954	0°1023	0°2321	0°2364

Zirconium and Neodymium.

Zirconium oxide—		Neodymium oxide—		Combined oxides—	
Found	Required	Found	Required	Found	Required
0°1349	0°1341	0°0413	0°0457	0°1762	0°1798
0°1439	0°1341	0°0973	0°1142	0°2412	0°2487
0°1372	0°1341	0°1102	0°1142	0°2474	0°2487
0°1446	0°1341	0°0952	0°1142	0°2398	0°2487

Zirconium and Praseodymium.

Zirconium oxide—		Praseodymium oxide—		Combined oxides—	
Found	Required	Found	Required	Found	Required
0°1317	0°1341	0°0420	0°0458	0°1737	0°1799
0°1344	0°1341	0°1099	0°1144	0°2443	0°2485
0°1312	0°1341	0°1129	0°1144	0°2441	0°2485
0°1304	0°1341	0°1014	0°1144	0°2318	0°2485

Thorium and Lanthanum.

Thorium oxide—		Lanthanum oxide—		Combined oxides—	
Found	Required	Found	Required	Found	Required
0°1254	0°1247	0°0407	0°0409	0°1661	0°1656
0°1222	0°1247	not det.	0°1023	—	—
0°1246	0°1247	0°1035	0°1023	0°2281	0°2270
0°1243	0°1247	0°1034	0°1023	0°2277	0°2270

Thorium and Neodymium.

Thorium oxide—		Neodymium oxide—		Combined oxides—	
Found	Required	Found	Required	Found	Required
0°1254	0°1247	0°0464	0°0457	0°1718	0°1704
0°1232	0°1247	0°1146	0°1142	0°2378	0°2389
0°1242	0°1247	0°1142	0°1142	0°2384	0°2389
0°1242	0°1247	0°1129	0°1142	0°2371	0°2389
0°1248	0°1247	0°1118	0°1142	0°2366	0°2389

Thorium and Praseodymium.

Thorium oxide—		Praseodymium oxide—		Combined oxides—	
Found	Required	Found	Required	Found	Required
0°1253	0°1247	0°0471	0°0458	0°1724	0°1705
0°1214	0°1247	0°1147	0°1144	0°2361	0°2391
0°1238	0°1247	0°1160	0°1144	0°2398	0°2391
0°1246	0°1247	not det.	0°1144	—	—

It will be noticed that the results with zirconium are not so satisfactory as those with thorium. This cannot be attributed to any difference in manipulation for they were obtained under similar conditions, the usual practice being to carry on the six separations at one time.

A tendency on the part of zirconium to resist separation from other elements is again indicated here. This tendency is exhibited by its precipitation being retarded by the presence of another element, and by the fact that when once brought down it frequently is contaminated by that element. In the attempts to separate zirconium from thorium by *m*-chloraniline, it was repeatedly noticed that conditions of digestion, sufficient to cause precipitation of zirconium by itself, were inadequate when thorium was present, and when the precipitate was thrown down it was badly contaminated with thorium. Similar observations were made when formin was used to effect their separation; in that case all of the thorium came down with the zirconium under conditions which failed to precipitate thorium when alone. It might be supposed that this peculiar behaviour of zirconium would not be noticed upon passing from thorium to the more basic elements, but a number of the results obtained in connection with lanthanum and praseodymium show incomplete precipitations

of zirconium, while neodymium was so inclined to come down with zirconium that a satisfactory separation could only be expected when all possible precautions had been taken to prevent it.

The oxides obtained by ammonia from the filtrates weighed less in the separations from zirconium than in those from thorium. If one attempts to attribute this difference to the greater solvent action of the filtrates from the zirconium, the only respect that suggests itself in which the two sets of filtrates differed is that they probably contained different amounts of the precipitant, *p*-toluidine. More of this reagent was necessary to effect a precipitation in the solutions containing thorium than in those in which zirconium was present, and it is probable that in carrying out the two precipitations, as was done in each instance, considerably more *p*-toluidine accumulated in the filtrates from the thorium. Sufficient attention was not given to this point while the determinations were being made to warrant an opinion as to the extent of its influence and it is merely offered as a possible explanation. As both the first and second precipitations were usually made from about 100 c.c. of solution, the combined filtrates and washings, in which the precipitations by ammonia were made, were of considerable volume, and the question of the solvent effect of all this solution upon the precipitate produced by ammonia presented itself at the time of the determinations. The final filtrates were usually partially distilled, the bulk of the alcohol and ammonia being obtained in the distillate, from which the alcohol was recovered. More ammonia was repeatedly added to the undistilled portions to see if further precipitation would take place. In a few instances the entire solution was evaporated to dryness and the residue ignited and weighed. The weights obtained substantially made good the discrepancies between the combined oxides "obtained" and "required," but as no blank determinations were made it was not proved that some of this may not have come from extraneous sources.

As previously stated, the recorded results were obtained by the use of the blast-lamp till practically constant weights resulted. The writer is of opinion, however, that errors may have occurred in this connection due to a constant composition not always being obtained, especially with lanthanum, neodymium, and praseodymium. The weights obtained, by blasting the first two, were frequently 10 per cent lower than those obtained by igniting over a Bunsen burner; there was less difference with praseodymium. Hitchcock found that neodymium and praseodymium sesquioxides by gentle ignition with free air access, gradually took on oxygen till the weights approximated those represented by the formula M_2O_7 (*Journ. Am. Chem. Soc.*, xvii., 525).

Herzfeld ("Chemie der seltenen Erden," p. 63) speaks of neodymium oxide as having a blue colour and assigns to it the composition Nd_2O_3 , and again (*Ibid.*, p. 122), in an abstract from Shapleigh's investigation, mentions a suboxide as a grey powder and a peroxide as a dirty grey powder. The oxide obtained in the present investigation was invariably of a light brown colour resembling cocoa powder, after ignition with the Bunsen burner, and was usually changed to a light blue or light purple colour by blasting. It was often necessary to pulverise and blast a long time before the bluish colour was uniformly obtained; indeed, in some instances part of the oxide still retained the cocoa colour, even though by excessive blasting practically no change in weight resulted. In view of the inadequate and somewhat conflicting information concerning neodymium oxides, the composition of the oxide obtained in any particular case must receive careful attention. The change of colour produced by blasting the lanthanum and praseodymium oxides was not sufficient to indicate a change in composition, but the weights, especially with lanthanum, were considerably reduced and the certainty of a definite composition should also be established in this instance.

The most that was attempted, during the present work, with any of the oxides, was to compare the weights obtained in the course of the analyses with those obtained

by direct precipitation from the aqueous solutions by ammonia, and blasting until they were constant within a few tenths of a milligram. It would seem as though the oxides obtained in this manner would be of constant composition, but it is not improbable that small variations may have occurred, and that lack of nice conformity may occasionally be attributed in part to this cause. The mechanical condition of the oxides previous to blasting was not always the same, and it seems not improbable that this fact may be of some importance where intense blasting is resorted to in order to remove the last traces of oxygen necessary to effect a complete transition from an oxide which, for example, is stable at the temperature reached by the Bunsen burner to one of a lower state of oxidation which may be the stable form at the temperature produced by the more intense heat of the blast-lamp. Judging from the experience of Hitchcock, and from the fact that blasting invariably reduced the weights, it seems probable that, in the case of some of the elements, at least, an oxide of a higher state of oxidation was more stable over the Bunsen burner than over the blast-lamp. Such behaviours have been noticed with some of the more common elements.

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.*

By L. M. DENNIS and J. G. ONFILI
(Concluded from p. 18).

In the series of experiments described in the following pages, the analyses were carried out in a "simple" Hempel burette provided with a water jacket, and water was used as the confining liquid.

Experiments were first made to ascertain whether benzene vapour mixed with air can be quantitatively absorbed by the ammoniacal nickel solution just described. The gas mixture was first passed into a pipette containing the ammoniacal nickel solution and was shaken with that reagent for three minutes. It was then drawn back into the burette, passed into a pipette containing mercury and 5 c.c. of 5 per cent sulphuric acid, and was shaken for three minutes, being then drawn back and measured.

TABLE III.

	I C.c.	II C.c.	III C.c.
Air taken	52.7	48.6	51.3
Air plus benzene	56.4	52.4	55.2
After shaking with ammoniacal nickel nitrate solution . . .	53.2	49.0	51.9
After shaking with 5 per cent sulphuric acid	52.7	48.6	51.3
Benzene taken	3.7	3.8	3.9
Benzene found	3.7	3.8	3.9

The above results show that benzene vapour is quantitatively absorbed by treatment with an ammoniacal nickel solution prepared as above, when the gas mixture is shaken with the reagent for three minutes. Results of approximate accuracy can be obtained by using a simple burette without water jacket, but there seems to be a slight heating of the gas mixture resulting from the absorption of the ammonia gas by the dilute sulphuric acid, this rise in temperature being sufficient to cause appreciable error in the final reading. To ascertain whether the time necessary for the absorption of the benzene could be reduced, other mixtures of benzene and air were prepared and were shaken with the absorbent for one minute, for two minutes, and for three minutes. The results, which need not here be inserted, showed that a three-minute shaking of the gas mixture with the absorbent is necessary for the complete removal of the benzene.

The next point to be ascertained was whether the nickel solution would absorb other constituents of illuminating gas, and would so interfere with their determination as to render its use for the absorption of benzene impossible.

Measured amounts of carbon dioxide were mixed with measured amounts of air, and this mixture was passed into a pipette containing the nickel solution. As was to be expected, the carbon dioxide was completely removed. It had already been found that the nickel solution had no effect upon air, and consequently the absorption of oxygen in the illuminating gas by this reagent did not need further examination. To ascertain whether carbon monoxide and the unabsorbable residue, consisting chiefly of methane, hydrogen, and nitrogen, is affected by the nickel solution, the heavy hydrocarbons were removed from 100 c.c. of illuminating gas by means of fuming sulphuric acid and potassium hydroxide, and the residue was then shaken for three minutes with the nickel solution and then with the dilute sulphuric acid. No diminution in volume resulted. From these experiments it appears that the ammoniacal nickel solution beyond removing, wholly or in part, the hydrocarbons other than methane, absorbs no other gas except carbon dioxide, but the fact that this last-named gas is removed by the reagent makes it impossible to use the nickel solution for the removal of benzene and allied carbons, and still adhere to the order that is usually followed (Hempel-Dennis's "Gas Analysis," 1902, p. 282). In the customary procedure the hydrocarbon vapours are first absorbed by alcohol, then carbon dioxide by caustic potash, and then the so-called heavy hydrocarbons by fuming sulphuric acid. Hempel and Dennis state that carbon dioxide may not first be removed by means of potassium hydroxide because benzene is soluble in that reagent (*Ibid.*, p. 281). Experiments were made to ascertain whether this statement is correct. A measured volume of air was mixed with a measured volume of benzene vapour, and this mixture was passed over into a pipette containing potassium hydroxide. No diminution in volume resulted. It therefore appears that the absorption of carbon dioxide by potassium hydroxide may properly precede the absorption of benzene. To be perfectly sure upon this point, however, the following experiment was made:—Three Muencke wash-bottles containing clear barium hydroxide solution were connected together and illuminating gas was passed through this chain. The carbon dioxide present in the gas was completely removed by the reagent in the first bottle. The gas issuing from the third bottle was therefore free from carbon dioxide, but could safely be assumed to contain some of all of the other constituents of illuminating gas. 100 c.c. of the gas issuing from the third bottle was drawn off into a Hempel burette and was then passed over into the caustic potash pipette. No decrease in volume took place. A repetition of this experiment gave the same result, and there was thus obtained confirmation of the statement made above, that potassium hydroxide removes nothing from illuminating gas except carbon dioxide.

Experiments were next undertaken to ascertain, if possible, the nature of the hydrocarbons removable by alcohol and by the ammoniacal nickel solution. These hydrocarbons probably consist largely of ethylene, propylene, and benzene. Ethylene was prepared by treating pure ethylene bromide with a zinc-copper couple. The purity of the gas was tested by passing it into fuming sulphuric acid, the confining water in the burette having first been saturated with the ethylene. Ten c.c. of the gas left a residue of 0.2 c.c. showing a purity of 98 per cent. Measured volumes of air were now mixed with measured volumes of this gas, and the mixture was then passed into a pipette containing the nickel solution and then into a pipette containing mercury and 5 c.c. of 5 per cent sulphuric acid. The results obtained were:—

TABLE IV.

	I. C.c.	II. C.c.	III. C.c.
Air taken	49.2	51.5	48.0
Air plus ethylene	58.0	60.8	54.2
After shaking with ammoniacal nickel nitrate solution . . .	58.8	60.1	55.1
After shaking with 5 per cent sulphuric acid	57.9	60.0	54.2

* From the *Journal of the American Chemical Society*, xxx, No. 3.

It therefore appearing that ethylene is not taken up by the nickel solution, experiments were next carried out to ascertain whether benzene and ethylene could be separated by means of the nickel solution. The results of these experiments follow:—

TABLE V.

	I. C.c.	II. C.c.	III. C.c.	IV. C.c.
Air taken	50.2	60.7	48.9	54.4
Air plus benzene	53.0	64.2	51.1	57.2
Air plus benzene plus ethylene ..	57.6	68.7	57.2	64.4
After shaking with ammoniacal nickel nitrate solution and then with 5 per cent sulphuric acid	54.7	65.2	54.9	61.6
Benzene taken	2.8	3.5	2.2	2.8
Benzene found	2.9	3.5	2.3	2.8
After shaking the residue with absolute alcohol and then with water	53.4	64.6	54.7	61.1
After treatment with fuming sulphuric acid and then with potassium hydroxide	50.7	61.3	49.7	55.3
Ethylene taken (88 per cent pure)	4.6	4.5	6.1	7.2
Ethylene found by alcohol	1.3	0.6	0.2	0.5
Ethylene found by fuming sulphuric acid and potassium hydroxide after alcohol	2.7	3.3	5.0	5.8
Total ethylene found	4.0	3.9	5.2	6.3
Ethylene taken (corrected volume)	4.04	3.9	5.36	6.3

The results in Table V. show that a satisfactory separation of benzene from ethylene and probably from the other hydrocarbons of the ethylene series may be effected by first shaking the gas mixture with the ammoniacal nickel nitrate solution for three minutes, and then with a 5 per cent solution of sulphuric acid for the same length of time.

It was hoped that it might be possible to remove the ethylene series of hydrocarbons by means of absolute alcohol before subjecting the illuminating gas to treatment with fuming sulphuric acid. If this were possible, the hydrocarbons would be divided, analytically, into three distinct groups, and a much clearer idea of the illuminants in the gas could then be obtained from the results of a volumetric analysis than is possible under the present methods. The results in Table V. have shown that the absorption of ethylene by alcohol is far from complete, and, moreover, that the results of such absorption are by no means constant. It was thought desirable, however, before abandoning the separation by alcohol to try the method with illuminating gas, and in Table VI. the results of these experiments are given.

TABLE VI.

	I. C.c.	II. C.c.	III. C.c.	IV. C.c.
Carbon dioxide	1.2	1.2	1.1	1.1
Benzene by nickel solution and dilute sulphuric acid	1.2	1.0	1.0	1.0
Hydrocarbons removed by absolute alcohol and water	1.5	0.3	1.3	0.5
Heavy hydrocarbons removed by fuming sulphuric acid and potassium hydroxide	2.3	3.5	2.6	3.4
Total hydrocarbons absorbed by the three reagents	5.0	4.8	4.9	4.9

These results demonstrate conclusively that absorption by alcohol can not be employed for the purpose in hand, and that at the present time the gas analyst must content himself with the absorption of benzene by the nickel solution and the subsequent absorption of the so-called heavy hydrocarbons by fuming sulphuric acid. In Table VII. are given four analyses of illuminating gas, showing the accuracy of the determinations of carbon dioxide, benzene, and the heavy hydrocarbons.

TABLE VII.

	I. C.c.	II. C.c.	III. C.c.	IV. C.c.
Carbon dioxide	1.2	1.2	1.2	1.2
Benzene by nickel solution and dilute sulphuric acid	1.0	1.0	0.9	0.9
Heavy hydrocarbons removed by fuming sulphuric acid and potassium hydroxide	4.0	3.9	3.9	4.0
Total hydrocarbons	5.0	4.9	4.8	4.9

Before the ammoniacal solution of nickel nitrate and the 5 per cent solution of sulphuric acid are used for the absorption of benzene, the reagents should, of course, be saturated with the other constituents of the gas mixture in the usual manner (Hempel-Dennis's "Methods of Gas Analysis," 1902, p. 119). If the reagents in the pipettes have been used for analysis of illuminating gas, they should not be used in the examination of generator gas or of any other gas mixture differing appreciably from the illuminating gas, for the gases that have been dissolved by the reagent when it was shaken with the illuminating gas would escape into another superimposed gas mixture, if this latter did not contain these dissolved gases at approximately the same partial pressure as that at which they existed in the gas with which the reagent was first shaken. Consequently the gas pipettes should be filled with fresh solutions of ammoniacal nickel nitrate and sulphuric acid whenever the gas mixture to be analysed differs markedly from that for which the reagents had previously been used.

The results may briefly be summarised as follows:—

1. Under the described conditions, alcohol does not completely remove either benzene or ethylene from gas mixtures.

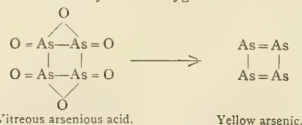
2. The use of an ammoniacal solution of nickel nitrate furnishes a rapid and exact method for the determination of benzene in mixtures of that substance with air and ethylene, and in coal gas.

The authors would recommend that in the analysis of illuminating gas (coal gas), the order of procedure be:—

(a) The absorption of carbon dioxide by potassium hydroxide; (b) the absorption of benzene by the ammoniacal solution of nickel nitrate above described; (c) the absorption of the "heavy hydrocarbons" by fuming sulphuric acid; (d) the absorption of oxygen by alkaline pyrogallol or by phosphorus; (e) the absorption of carbon monoxide by cuprous chloride; and (f) the determination of the methane and hydrogen.

The authors have been unable to try this new method on any commercial gas mixture other than the local supply of illuminating gas. They would therefore earnestly request chemists using the method on other gas mixtures to communicate to them the results of such analyses and call their attention to any difficulties that may arise.

The Constitution of Sesquioxide of Arsenic.—H Erdmann.—By reducing vitreous arsenious acid with zinc powder in the presence of sulphide of carbon and of saline solutions, such as solutions of borax, chloride of ammonium, and chloride of magnesium, we obtain a small quantity of yellow arsenic (see below). The author, having shown that this yellow arsenic corresponds to a molecular weight of As_4 , arrives at the formula As_4O_6 for arsenious acid. In this body the atom of arsenic appears to be pentavalent; it becomes trivalent by loss of oxygen.



THE THERMO-CHEMISTRY OF THE THEORY OF ELECTROLYTIC DISSOCIATION.*

By JOSEPH W. RICHARDS.

Heat of Ionisation.

THE theory of electrolytic dissociation assumes that in dilute solutions of electrolytes the salts are already potentially split up into their positive and negative ions. The first time that I read this statement of the theory, my first thought was:—"Where does the energy come from to cause this dissociation?" This query has been firmly lodged in my mind ever since, and has not been satisfactorily answered by the numerous treatises on electrochemical theory which have since appeared.

The heat of solution in excess of water is usually not a large quantity. The molecular heat of formation of solid potassium chloride is, for instance, 105,700 calories, while if this is dissolved in excess of water 4500 calories are absorbed. If, then, we assume that the solid salt is composed of undissociated molecules, and the dilute solution of ionised molecules only, then the heat absorbed in the process of ionising the solid molecules cannot be over 4500 calories, and therefore bears no quantitative relation at all to the heat of formation of the solid molecules. In fact, we have been overlooking the physical change of state, for the solid salt certainly absorbs heat in changing to the liquid or gaseous molecule in which it occurs in solution, and this change is responsible for part of the 4500 calories absorbed in the act of solution. The heat of ionisation of undissociated molecules of KCl in solution into completely ionised molecules can therefore be but a part of 4500 calories, if it has any real value at all, and the ultimate conclusion is evident that, whatever the energy required to ionise molecules of salt in solution may be, it is not of the same order of magnitude, nor can it be in any way identified with the heat of formation of the salt from its constituent elements. It follows that the act of ionisation, whatever it may be, is certainly not a destruction or dissociation of the compound *qua* compound, but that from the energy standpoint potassium chloride is as really a compound of potassium and chlorine when ionised in dilute solution as when in the solid condition.

There has been a great deal of uncertainty about this question, and the leading exponents of the dissociation theory leave the subject in a very hazy condition. To remedy this, we must stop thinking that a molecule ceases to be a compound when it is dissolved in dilute solution, or ionised. Whatever the ions are, they are not the chemical constituents from which the compound was formed, and the separation of the molecule into ions is not a destruction of the compound or a resolution of it into its chemical constituents. Ostwald says in his "Grundlinien der Anorganischen Chemie," 1900, p. 210:—"Auch in festen salzen, die nicht elektrolitisch dissoziirt sind, befinden sich die Bestandtheile dem Ionenzustand viel näher, als dem der freien Elemente. Dies geht daraus hervor, dass der Uebergang der festen Salze in den Ionenzustand bei der Auflösung in Wasser im allgemeinen nur unbedeutende Wärmewirkungen (meist sogar Wärmefreisetzen) ergibt." In other words, Ostwald recognises that since solid salts, which are not electrolytically dissociated, dissolve in water with very slight thermal effects, that the solid molecule of an undissociated compound is nearer to the ionised condition than to the constituent elements from which it was formed. If we turn this statement around, it is that the condition of complete ionisation is much nearer to the undissociated solid molecule than it is to the free constituent elements of that molecule.

What then is the ionised condition? We can say with certainty, for one thing, that it is a condition of the compound, and not a condition in which the compound has ceased to exist and is resolved into its constituent elements.

What is then the heat of ionisation? It is the heat absorbed in a change of state of the compound, and is, as far as we can gather, more a physical change of state than a chemical one. It must not be confounded with the heat of solution, for that includes the change of state from the solid molecule to the dissolved ions: neither can it be completely identified with the heat of dilution, for while during dilution molecules in solution become ionised, yet there are possibly other operations included, such as the making or decomposing of hydrates in solution, and the heat of solution is thus seen to be also a complex quantity.

Arrhenius has calculated heats of ionisation theoretically from thermodynamic considerations, from the change in value of the dissociation constant with temperature. He makes them to be negative quantities even in case where the heat of dilution is positive. It therefore would follow, if these calculations are to be relied upon, that the heat of dilution consists of an absorption of heat due to ionisation plus an evolution of heat due to combination with water. In any case, we are no nearer the solution of the riddle than before.

There is one thermochemical law which gives us pretty firm ground to build upon, viz., the observation that the heats of formation of salts in dilute solution are plainly additive in their nature. This means that the heat of formation of potassium chloride, for instance, is composed of the sum of one value characteristic of potassium and one characteristic of chlorine. All potassium salts therefore differ from all sodium salts, in their heat of formation to dilute solution, by a constant difference—the difference between the constants of potassium and of sodium; while all chlorine salts differ from all bromide salts by a constant difference—the difference between the constants of chlorine and of bromine. This law is in general true, and places the thermochemical constants of the heat of formation of salts to dilute solutions in exactly the same category as the equivalent electrical conductivities of dilute solutions, their specific gravity, specific optical refractive power, and some other physical properties. The truly additive nature of the heats of formation of salts in dilute solutions is a law of the deepest meaning for thermochemistry.

If we consider a dilute solution as containing only ionised molecules, then the heat of formation may be considered, in light of the above thermochemical law, as simply the sum of the heats evolved in the passage of each constituent of the salt from its ordinary molecular condition into the state of being a dissolved ion. The thermochemical constant of a metal would then be regarded as the heat evolved in its passage from the ordinary molecular free state into the state of combination as a dissolved ion. This quantity has been called by Ostwald the *ionisation heat* of the elements, which, it will be observed, is using the term with an entirely different meaning than was given it, as we have been so far considering it. The ionisation heat of a compound is the heat necessary to resolve its dissolved un-ionised molecule into its ions—which operation is not a resolution of the compound into its constituents, and has therefore nothing to do with the heat of formation of the compound. The ionisation heat of an element is the heat given out in changing it from a free, molecular element into the state of a combined dissolved ion. The act of combination is involved in the latter act of ionisation, and the term ionisation here no longer refers to the electrolytic dissociation of the compound.

Considering the term "ionisation heat of the elements," in the sense above given to it, and further considering it as equivalent in value to the thermochemical constants of the elements, we are led to some interesting conclusions. It would follow from this that elements exist in two conditions, viz., the uncombined state and the combined state. Passage into the combined state is accomplished by a change in the intrinsic energy which is characteristic once for all of the element, for a given valency, and independent of any reciprocal action towards the other element or elements with which it is combined; and this combined state is only perfectly attained in dilute solution. Ions in solution are

* A Paper read at the Fourth General Meeting of the American Electrochemical Society, at Niagara Falls, September 19, 1903.

in this view atoms of the element which have passed completely into the "combined" condition, and in doing so have given out their contribution towards the heat of formation of the compound.

The heats of formation of salts to dilute solutions always give us the sum of the separate heats of combination of its separate ions and their "heats of ionisation." (K, Cl, aq.) = 101,200 calories expresses the fact that the sum of the heats evolved by 39 grms. of solid potassium becoming ionised and 35.5 grms. of chlorine gas becoming ionised, is that many calories. (K₂, S, O₂, aq.) = 274,600 calories expresses the sum of the heats of ionisation of 2K-solid and of SO₂ gas (assuming those to be the ions), plus the heat of formation of SO₃ gas. The only difference between the thermochemical constants and the heats of ionisation would be in the case of complex ions such as SO₃, for instance, in which case the thermochemical constant for SO₃ would be its heat of ionisation (*i.e.* passage from the state of SO₃ gas to SO₃ ion in dilute solution) plus the heat of formation of SO₃ gas from its elements.

In a few cases, such as iodine and mercury, we know approximately the amount of heat necessary to convert the ordinary free element into atoms. I₂ gas = 2I gas absorbs 28,500 calories, but takes place only at a red heat. Hg (liquid) = Hg (monatomic gas) absorbs 13,560 calories, taking place at 355°. We may therefore go slightly further than Arrhenius in these cases, and say that if Hg (liquid) = Hg ion + 20,500 calories, that therefore Hg (monatomic gas) = Hg ion + 20,500 + 13,560 = +34,060. This calculation is not exact, because the latent heat of vaporisation of mercury at 18° is not exactly the same as at 355°, being probably somewhat greater. This quantity would be the real heat of ionisation of the element, that is, the heat evolved in conversion of one free gaseous atom into one combined dissolved ion. If this could be determined for a number of elements, it is very likely that some generalisations might become evident. This is the only basis on which the true ionisation heats of elements can be determined, and to deduce them from present data we must know more of the latent heats of fusion and of volatilisation of the elements.

(To be continued).

A PROPOSED METHOD OF TESTING WOOD TREATED TO RESIST FIRE.*

By CHAS. F. McKENNA.

IN the spring of 1902 an effort was made by the Bureau of Buildings of the Borough of Manhattan, New York City, to secure more certitude as to the qualities of the so-called fireproof wood which was being delivered in the city for use in high buildings.

Methods of test which have been in vogue for some time in the Bureau of Buildings were stated to be inadequate for the proper discrimination between well-treated wood and that which was treated only imperfectly and was presumably at times not fireproof in any sense. These methods included the test, long in use in the Navy Department, of exposing shavings to the influence of heat while they rested upon a wire screen, timing the rate of combustion, as well as estimating its extent; also the splinter test as practised in the simple expedient of holding a splinter of wood in and across the flame of a Bunsen burner or upon a red-hot iron plate; also, what may be called the cob-work test, by which prisms of wood about six inches long and one inch, more or less, square, are piled with air-spaces between them and exposed to the flame of a Bunsen burner. There was finally the more meritorious test of Professor Woollen, of Columbia University, which he calls the timber test, in which specimens of wood one inch square and one foot long are laid in pairs across the top of

a 6-inch gas furnace and exposed to a presumably constant temperature of 1700° F. The depth to which the specimens were charred was subsequently measured and the unburned area used as a basis of comparison.

The fundamental fault with all of these methods of test lies in their neglect of the chemical factors involved in the decomposition of wood under the influence of heat. Nor were proper attempts made to standardise the conditions governing the application of the flame, the access of the air, and the surrounding temperatures, &c. Again, no instrumental means of registering the differences in the results obtained were suggested. In the timber test, the accurate measure of the unburned area does not answer this need, and fails of its purpose where the conditions during the test have so varied.

In the course of the discussion upon this subject which took place about the time mentioned in New York City, there was found to be a demand for an "inspector's test"; that is, for an instrumental and simple test giving results measurable and free from guess and which could be carried on at the place of delivery of the timber. The writer approached this subject from the chemist's side, and his first effort was to undertake distillation tests in closed retorts.

Inasmuch as it was early admitted that these fire-proofing processes could not prevent the destruction of wood by fire operating under its worst aspects, but could only stay the disintegrating effects long enough to present the hope of gaining some advantage over the demon, it seems strange that the search for this test did not then take the form of a study of the reactions proceeding during the inflammation and combustion of the wood, as well as of those accompanying its destructive distillation for the purpose of finding facts leading to more certain means of measuring the retarding values of the various treatments to which wood is subjected for this purpose. The writer outlined such a study by means of destructive distillation of samples of natural and of treated woods; for, although combustion and inflammation with free access of air are undoubtedly the most common conditions of a conflagration, yet the breaking down of the cellulose molecule, of the fundamental tissues of the wood, as well as of its allied organic and mineral constituents, takes place from the centre of large masses as a distillation without air, just as it does also when timber and planking burn at the back of a hot brick wall, or within a metal-cased door or window frame, or where electric wiring passes over wood encased in concrete flooring or in walls. The prosecution of such studies has been stayed through lack of means, but the initial efforts nevertheless have resulted in this proposed method of testing which, with the apparatus offered, seems to be the means for easily making an extended series of critical observations.

Some early distillations made upon charges of wood shavings in 6-ounce glass retorts heated by a triple Bunsen burner developed the fact that when the temperature reaches 250° C. the volatile products cease to be driven off, and temporarily a vacuum is produced if the heat is not promptly raised. This took place in every case in not over three minutes of such heat conditions, and also, under the same conditions, the yield of gas was quite uniform for different woods. To secure higher temperatures in a brief time, the electric wire method was adopted. This led to the invention of an electric test retort, and this in turn, when tried on numerous lots of wood, quickly developed the fact that the little instrument was exactly adapted to meet all the requirements of an inspector's test when the original untreated wood is at hand to compare with the treated, and perhaps also where original samples cannot be obtained. This apparatus is described in my paper presented at this meeting under the title "Electric Test Retort."

In using it for the study of fireproof-wood, it has been my aim to simplify it, as well as the details of the testing, in order that numerous samples of wood could be examined easily and quickly.

A large gas burette was provided, having with it a large reservoir for levelling, and this in connection with the electric test retort were all that I found necessary for making critical tests of treated woods. Absorption tubes for the pyrolygineous products could be provided, but in the work in hand the necessity was obviated as much as possible by the high initial heat and by providing that the water in the gas burette shall absorb the pyrolygineous products until nearly saturated with them.

Violette, as quoted by Sadtler ("Handbook of Industrial Organic Chemistry," second edition, p. 334) in studies devoted to distillation of wood, found that when it is slowly heated the water and pyrolygineous acids, alcohols, and creosote are all driven off up to and at 280° C. to the extent of 63.8 per cent of the original weight; a large volume of gas up to and at 350° C.; and up to and at 430° C. a total loss of weight of 81 per cent is experienced. But quickly heated wood placed at once in the retort at 432° C. lost 91 per cent. Senff (*Ber. d. Chem. Ges.*, xviii., 60) in distilling a variety of woods in 100 kg. charges, found that the uncondensed gases in slowly heated samples varied from 17.17 per cent to 29.23 per cent with an average of 22.64 per cent for fifteen examples of different woods; the uncondensed gases resulting from quickly heated samples varied from 24.07 per cent to 35.56 per cent, with an average for fifteen samples of 31.50 per cent. He found that the charcoal varied from 23.23 per cent to 34.68 per cent, with an average of 27.59 per cent in slowly heated samples, and from 20.20 per cent to 31.59 per cent, with an average of 23.09 per cent, in quickly heated samples. He also found the very important fact that the more common woods, as oak, beech, birch, poplar, and pine, show by the results of the destructive distillation that they resemble one another very much in fundamental composition and give like results in the yield of the respective products.

Hence, we should have in the electric test retort an opportunity to heat quickly to the highest temperature, thus obtaining the maximum gas yield. Fortunately, also, in this test retort, it is not strictly a distillation without access of air; it is really, in a small way, quite a perfect duplication of conditions existing at the beginning of a fire in a closed space, and we have also in this apparatus an opportunity to introduce air in measured quantities, if required.

In conducting the test, a small charge of wood, cut as a little cylinder about 0.5 inch long and 0.25 inch wide, weighing about 500 mg., is placed within the platinum wire basket, the dome is placed upon the apparatus and clamped tightly by suitable means, and the tube leading off from the dome is connected to the gas measuring burette having the usual reservoir tube attached. A current at a difference of potential of 120 volts and a strength of from 7 to 12 amperes is used. Great precautions are needed to keep the current strength steady, and a 7.5 ampere current is the best strength for this experiment. Tests made with the Le Chatelier pyrometer show that the temperature within the coil with a 7.5 ampere current is 680° C.; with a 10 ampere current the temperature rises at the end of three minutes to 840° C. The charge of wood is subjected to the effects of a current of 7.5 amperes for exactly two minutes, the gas being conducted to the burette. Observations of the glow, if any, and of the amount of smoke and the character of same, can all be made and recorded. At the close of the two-minute interval, the current is shut off, the gas burette stop-cock closed, and air admitted to the retort by opening the tubulure at the side. The gas in the burette is cooled, and the volume measured. Or, if a series of tests are being made, the conditions of which are known and invariable, the volume could be read without correction, where so noted. So also, the correction for the volume of air increased by the heat of the contents of the retort can be neglected, for it will be found to be a very constant figure under uniform conditions. Thus, with some experiments in blanks, in heating without the charge with a 7 ampere current for two minutes, the results were 23.6, 22.8, 22.8, 22.6, 22.6 c.c. With the 6.5 ampere

current for two minutes, the results were 21.6, 21.6, and 21.6 c.c. Other experiments gave, with a 7 ampere current for two minutes, 21 c.c. average; with a 7.5 ampere current for two minutes, 24 c.c. average; with an 8 ampere current for two minutes, 26.5 c.c. average; and others with an 8 ampere current for two minutes, 26 c.c. average.

(To be continued.)

CORRESPONDENCE.

RADIUM.

To the Editor of the Chemical News.

SIR, — It may be worth while to place on record some observations I have made recently in experimenting with radium. I first of all attempted to produce the "scintillations" on a new blende screen by means of radium contained in a sealed glass tube, not knowing at the time that they cannot be caused in this way; but after waiting in the dark for some minutes, I noticed a kind of scintillation resembling occasional meteors on a dark sky, and I have always observed the same appearance (without the tube of radium salt), although the screen had never been brought near radium without intervening glass, and although in some cases the screen had been left for several weeks untouched. I would suggest that these slight scintillations are caused by a spontaneous change in the structure of the blende crystals, which is always taking place, and that the change is brought about suddenly by the impact of the minute particles in the α -rays.

If radium-barium bromide (I have used 0.1 per cent) is sprinkled on a blende screen, the effect, seen through a magnifying glass, is an appearance like a mass of luminous insects hard at work and quickly moving amongst each other. On shaking off the salt and gently tapping the screen to remove as much as possible, the appearance changes to that of a sky thickly studded with brightly twinkling stars.—I am, &c.,

E. P. PERMAN.

University College, Cardiff,
January 10th, 1904.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxvii., No. 24, December 14, 1903.

Direct Preparation of Cyclohexanol and Cyclohexanone from Phenol.—Paul Sabatier and J. B. Senderens.—The authors prepare cyclohexanol and cyclohexanone,—



directly from phenol. Reduced nickel is maintained at a temperature of 215–230°, and a mixture of vapour of phenol and excess of hydrogen passed over it. The hydrogenation of the radicle rapidly takes place, tending to produce cyclohexanol. A portion of this is dissociated by the action of the nickel giving the corresponding ketone. The two substances are separated by a delicate operation.

Action of a Mixture of Oxygen and Hydrochloric Acid on Certain Metals.—Camille Matignon.—In a preceding research the author showed that a mixture of oxygen and hydrochloric acid attacked gold, platinum, and tellurium at temperatures far inferior to the temperature of the oxidation of hydrochloric acid gas by oxygen. In the present research he generalises this reaction and finds that

pladium is attacked in the cold by this mixture. In the case of ruthenium, if this metal is placed with the mixture in a sealed tube at 125°, chlorination is complete in a few hours: Iridium at 150° is also attacked in eight to ten hours.

Constitution and Properties of Silicon Steels.—Léon Guillet.—The author investigates the constitution and mechanical properties of silicon steels, and shows that—(1) only steels containing less than 5 per cent of silicon can be utilised; (2) silicon steels offer a great resistance to shock after they have been tempered, this resistance is greater for steels rich in carbon; (3) certain anomalies exist between the constitution already established and that proved by the present research, in the case of industrial ferrosilicons and silicon steels, and notably the compound Fe_2Si ; (4) the author's researches, and also those of M. Osmond, seem to prove the existence of two solutions of silicon in iron, one probably having the constitution Fe-Si , the other $\text{Fe-Fe}_2\text{Si}$.

New Method of Determining the Critical Points of Irons and Steels.—O. Boudouard.—The author investigates M. Saladin's method of determining the critical points of steel and iron, and his method of utilising the calorific phenomena which accompany the molecular transformations of the metals.

Meteoric Iron.—F. Osmond and G. Cartaud.—The authors apply to meteoric iron their method of investigation utilised for the micrographical analysis of irons and terrestrial steels.

Preparation of Iridium Sesquiselenide.—C. Chabrie and A. Bouchonnet.—Of the four compounds of sulphur and iridium which have been described one only appears to have certain existence, the sesquisulphide. The authors, therefore, when investigating selenium compounds, endeavour to obtain the selenide corresponding to the sesquisulphide. This compound is prepared by a method analogous to that by which the sulphide is prepared; i.e., by passing a current of seleniuretted hydrogen into a solution of sesquichloride of iridium and slightly heating. The substance after purification is analysed, and is found to be similar in constitution and properties to the sesquisulphide.

Acetates of the Alkaline Earths.—Albert Colson.—To prepare the acetates of magnesium and calcium the author adds a sufficient quantity of acetic acid to the anhydride of the metal. In the case of magnesium the acetate $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 + 1.5\text{C}_2\text{H}_4\text{O}_2$ is formed, identical with that formed by adding metallic magnesium to glacial acetic acid.

Action of Bromosuccinic and Bibromosuccinic Acid on the Pyridic and Quinolic Bases.—Louis Dubreuil.—The action of pyridic and quinolic bases on the bromine derivatives of succinic acid vary with the nature of the base and that of the solvent. According to the circumstances, malic, fumaric, bromofumaric, bromomaleic acid, or bicarbonic acetylene, are formed.

A New Tri-iodine Phenol.—P. Brenans.—In previous researches the author prepared the di-iodine isomers of phenol, $\text{OH-C}_6\text{H}_3\text{I}_2$ 1.2.4, 1.2.6, 1.3.6, 1.3.5, and 1.3.4, as well as the nitro-benzenes and the iodine anilines from which they are prepared. He now describes the iodine compounds which are obtained from di-iodine orthonitroaniline, $\text{NH}_2\text{-C}_6\text{H}_2\text{I}_2\text{-NO}_2$ 1.4.6, by the following series of reactions:—1. The diazoic sulphate of this nitraniline is decomposed with potassium iodide, and changes into tri-iodine nitro-benzene, $\text{NO}_2\text{-C}_6\text{H}_2\text{I}_3$ 1.3.5.6. This nitrated derivative gives on reduction a tri-iodine aniline, $\text{NH}_2\text{-C}_6\text{H}_2\text{I}_3$ 1.3.5.6. This base is then diazotised, and the diazo compound heated in presence of water, giving tri-iodine phenol, $\text{OH-C}_6\text{H}_2\text{I}_3$ 1.3.5.6. The author describes the conditions under which these transformations take place and the properties of the new bodies.

Iodides of Mercur-ammonium of the Primary and Tertiary Amines.—Maurice François.—The iodides of mercur-ammonium derivatives of the amines have been

very little studied. The author's researches show that the iodides of mercur-ammonium derivatives of the primary amines form a series parallel to that of the derivatives of ammonia, in which, however, the hydrogen of the ammonium is replaced by mercury.

Stereoisomerism in the Substituted Campho-carbonic Ethers and Methyl-homocamphoric Acid. Ethyl Camphocarbonic Acid.—J. Minguin.

Etherification of Phosphoric Acid by Glycerin.—P. Carré.—The author establishes the fact that phosphorus acid forms with glycerin three ethers in air or vacuo—(1) a monoether, ordinary glycerol-phosphoric acid, a mono-acid to helianthine and a di-acid to phthalein; (2) a di-ether, mono-acid to helianthine and to phthalein; (3) a tri-ether neutral to indicators.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxix., No. 12.

The Electrolysis of Alkaline Sulphides.—André Brochet and Georges Ranson.—Already noticed.

The Electrolysis of Alkaline-earthly Sulphides.—André Brochet and Georges Ranson.—Already noticed.

The Electrolysis of Sulphide of Barium, with a Diaphragm.—André Brochet and Georges Ranson.—Already noticed.

Amide and Nitride of Barium.—MM. Guntz and Mentrel.—A fragment of barium placed in a U-tube through which a current of ammonia is passed, and plunged into a transparent melted bath of chloride of lithium and chloride of potassium in molecular proportions, does not show any change up to 280°. At this temperature, however, the metal becomes covered with a blackish liquid through which a large number of small bubbles of hydrogen pass. On raising the temperature the liquid becomes green, then red, and on cooling goes through these changes again in the inverse order. But a pure product cannot be obtained in this manner, as the liquid formed attacks the glass, and the tubes break before cooling. For this reason we used iron boats instead. These boats were at first heated in a glass tube over a naked flame, and similar phenomena were observed; but if, eventually, the temperature was raised to about 600°, still in a current of ammonia, the product solidifies, and the evolution of gas continues even when there is no longer any free barium left in the boat. These changes show that various reactions take place at different temperatures. To determine the nature of these changes, the authors have made a number of experiments at constant and known temperatures, using M. Guntz's electrical heating apparatus already described (*Bull. Soc. Chim.*, Series 3, vol. xxvii., p. 153). To prevent projections, and the consequent decomposition of the products on contact with the glass, the boats were surrounded with a thin sheet of iron or nickel. Experiment showed that at 280° hydrogen commenced to come off; the temperature can be raised to 380–400° without the liquid formed being decomposed on contact with the iron or nickel cover. On cooling, the mass appears as a greyish-white homogeneous substance, giving off ammonia in moist air. Three estimations of the total alkalinity and ammonia give:—

	I.	II.	III.	Calculated for $\text{Ba}(\text{N}_2\text{H}_2)_2$
$\text{NH}_3/\text{total alkalinity}$..	0.48	0.496	0.48	0.50

It must be remembered that these products contain all the impurities of the original barium. These figures correspond to the formula $\text{Ba} + 2\text{NH}_3 = \text{Ba}(\text{N}_2\text{H}_2)_2 + \text{H}_2$. This amide was obtained best by preventing the fused product from boiling. Further experiments were made on the decomposition of the amide in a current of ammonia gas, and *in vacuo*, when the nitride is formed.

Some Amino-magnesian Phosphates; Methyl-amino- and Trimethylamino-magnesian Phosphates.—Ch. Porcher and M. Brissac.—A solution of hydrochlorate of amine is mixed with a 10 or 15 per cent solu-

tion of disodic-phosphate in slight excess; on adding a solution of sulphate of magnesia, a slight crystalline cloudiness appears. This is dissolved by adding a few drops of hydrochloric acid and then the free base until strongly alkaline. Or the mixture of the hydrochlorate of the base and phosphate of soda can be made strongly alkaline, and the solution of sulphate of magnesia added gradually; the results obtained are the same whichever method is adopted. The precipitate obtained is left for twenty-four hours, filtered, washed carefully with water, alcohol, and ether, then drained and dried for a few minutes at 40° . This is the trimethylamino-magnesian phosphate. The trimethylamino-magnesian phosphate is prepared in a similar manner, using trimethylamine in the first instance.

Action of some Gases on Barium-ammonium.—MM. Guntz and Mentrel.—Inserted in full (p. 13).

Some Amino-magnesian Arseniates; Methylamino- and Trimethylamino-magnesian Arseniates.—M. Brissac.—The formation of the amino-magnesian arseniates corresponding to the above mentioned phosphates is brought about under the same conditions as for these latter, except that a greater alkalinity is necessary, and care must be taken not to use too much sulphate of magnesia.

Behaviour of Phenolphthalein in the presence of Bicarbonates and Alkaline Carbonates.—M. Giraud.—Inserted in full (p. 27).

The Use of Bin oxide of Lead in Analysis.—M. St. Bogdan.—Inserted in full (p. 26).

Some Reactions of Pinacolin and of Pinacone.—G. Deniges.—The author considered that pinacolin, in its character of a ketone, ought to give with sulphate of mercury a compound analogous to that he has already described with ordinary acetone and its homologues. This was found to be the case; on heating a drop of pinacolin with 5 c.c. of acid sulphate of mercury in a glass tube in a boiling water-bath, after a few minutes a yellow colour was observed which soon gave place to a heavy yellow precipitate in spheroidal crystals, corresponding to the expected compound. Other experiments gave similar confirmatory results. The results prove the ketonic formula of pinacolin, and consequently of the other pinacolins so closely related to it; further, they enable us to detect pinacone itself with ease.

The Nitric Ethers of the Acid Alcohols.—H. Duval.—Twenty-five grms. of pure white glycolic acid are ground up rapidly in 30 grms. of nitric acid of 1.45 density, and while keeping cool, 25 grms. of concentrated sulphuric acid are added; let stand, and pour the whole over 100 grms. of crushed ice and 50 grms. of water. Then extract successively with 100 c.c. and 50 c.c. of ether, taking care to keep the temperature down to 0° . The ethereal solution is washed with water until all the sulphuric acid has disappeared, then evaporated; the product, dried over sulphate of soda, is taken up with anhydrous ether, filtered, and finally placed *in vacuo* over sulphuric acid, where it crystallises in forty-eight hours. The return is over 37 per cent. Its formula is $\text{CH}_2\text{—ONO}_2\text{—CO}_2\text{H}$.

A New Di-iodised Phenol.—P. Brenans.—Already noticed.

Migration of the Methyl Group in the Camphor Molecule.—G. Blanc and M. Desfontaines.—Already noticed.

Precipitation of some Alkaloids by Nitrate of Uranium. Reaction of Morphine.—J. Aloy.—Inserted in full (p. 26).

Influence of the Nature of its Surroundings on the Degree of Hydration of a Plant.—E. Charabot and A. Hébert.—Not suitable for abstraction.

Attempts to make Aniline and Urea take the Form of Amino- (Anilino- or Ureo-) Magnesian Phosphate.—Ch. Porcher and M. Brissac.—The authors have found that as they deal with fatty amines richer in carbon, the amino-magnesian phosphate obtained loses its stability,

or even does not form at all. In this manner the accumulation of carbon in the amine tends to diminish the basic character which is so marked in the first ones.

MISCELLANEOUS.

Accidents in Tar Distilleries.—The attention of the Home Office has been directed by the reports of the Inspectors of Factories, and by the occurrence of fatal accidents, to the serious risks incurred by persons employed in works in which is carried on the distillation of tar for the production of naphtha, light oil, creosote, and pitch. It is thought desirable, pending a revision of the existing special rules for chemical works, to urge certain recommendations upon occupiers; these are for the most part based upon the precautions actually in use in certain works. The recommendations are nine in number, and are issued on "Form 919" from the Home Office, October, 1903. Instructions are also given for the resuscitation of persons who have been "gassed," and for the administration of oxygen.

Regulations for the Manufacture of Electric Accumulators.—These regulations were issued in draft by the Home Office on August 10, 1903, and no objection of substance (except those since withdrawn) was made by employers, by workmen, or by other persons affected. They have now been formally made by the Secretary of State, and issued in printed form, and will apply to such works on and after January 1, 1904. Besides these regulations, the Home Office has sent out a number of observations by way of explanation of certain of the regulations, and, further, to indicate additional safeguards which it has not been thought practicable to define as formal requirements. Copies of these regulations must be kept posted up in conspicuous places in all factories and workshops to which they apply. They can be obtained from Messrs. Eyre and Spottiswoode, East Harding Street, London, E.C.

MEETINGS FOR THE WEEK.

TUESDAY, 19th.—Royal Institution 5. "Development of Animals," by Prof. L. C. Miall, F.R.S.

Society of Arts, 8. "Celtic Ornament," by George Coffey.

WEDNESDAY, 20th.—Microscopical 8. Dr. Woodward's Presidential Address: "On the Evolution of Vertebrate Animals in Time."

Society of Arts 8. "Organ Design," by Thomas Casson.

Chemical, 5.30. "Optically Active Asymmetric Nitrogen Compounds, *d*- and *l*-Phenyl methyl ethyl zylammonium Salts," by H. O. Jones. "Chemical reactions of Nickel Carbonyl—Part I. Reactions with the Halogens, &c.; Part II. Reaction with Aromatic Hydrocarbons in presence of Aluminium Chloride, Synthesis of Alkylides and Anthracene Derivatives," by J. Dewar and H. O. Jones. "A Microscopical Method of Determining Molecule Weights," by G. Barger. "o-Nitrobenzoic Acid," by E. R. Needham and W. H. Perkin, jun. "The cis and trans-Modifications of α -Trimethylglutamic Acid," by W. H. Perkin, jun., and Miss A. E. Smith. "Influence of Nuclear Substitution on the Rate of Oxidation of the Side-chain—1. Oxidation of the Mono- and Dichlorotoluenes," by J. B. Cohen and J. Miller. "Simple Thermostat for Use in connection with the Refractometric Examination of Oils and Fats," and "The Interdependence of the Physical and Chemical Criteria in the Analysis of Butter-fat," by I. E. Thorpe. "Condensation of Furfuraldehyde with Sodium Succinate," by F. W. Litherley and J. F. Spencer.

THURSDAY, 21st.—Royal Institution, 5. "The Flora of the Ocean," by G. R. M. Murray, F.R.S.

FRIDAY, 22nd.—Royal Institution, 9. "Spectroscopic Studies of Astrophysical Problems at Stonhenge College Observatory," by the Rev. Walter Snyggars.

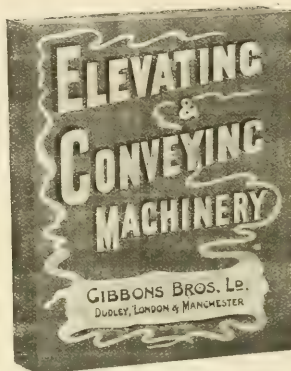
SATURDAY, 23rd.—Royal Institution, 3. "Brush Folk Song" (with Vocal Illustrations), by J. A. Fuller Matland, M.A.

LOSE no time in Writing for a Copy of our . .
NEW ILLUSTRATED CATALOGUE
 OF

**GIBBONS
 BROS., Ltd.**

MANCHESTER—

85 Trevelyan Bldgs.
 52 Corporation St.



**Dibdale Works,
 DUDLEY,
 WORCS.**

LONDON—

142-3 Palace Chmbs.
 Westminster, S.W.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
 JEWRY STREET, ALDGATE, E.C.

Principal—CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.

**EVENING CLASSES IN CHEMIS-
 TRY, METALLURGY, PHYSICS, and
 MATHEMATICS.**

Designed to meet the requirements of those engaged in
 CHEMICAL, METALLURGICAL, and ELECTRICAL
 INDUSTRIES,
 and in trades associated therewith.

Every facility for Special and Advanced Practical Work in well-
 equipped Laboratories.

CHEMISTRY	..	..	..	{	CHARLES A. KOHN, M.Sc., Ph.D., F.I.C., and G. SENTER, B.Sc., Ph.D.
PHYSICS	..	..	..	{	R. S. WILLOWS, D.Sc., B.A.
METALLURGY	..	..	..	{	C. O. BANNISTER, Assoc.R.S.M.
MATHEMATICS	..	..	..	{	G. W. . . KAYE, B.Sc.

CLASSES IN METALLURGY.

GENERAL METALLURGY.
 THE METALLURGY OF GOLD and SILVER.
 METALLOGRAPHY, including PYROMETRIC WORK.
 ASSAYING.

ANALYTICAL CHEMISTRY,

Including ELECTROLYTIC and GAS ANALYSIS.

Each Course of Lectures will be accompanied by suitable Laboratory Work.

GLASS BLOWING.

Two Courses of Instruction will be given during the Lent Term
 by Mr. A. C. COSSOR.

New TERM begins MONDAY, JANUARY 4th,
 1904.

The Institute is readily accessible, and near to Fenchurch Street,
 Liverpool Street, Broad Street, and Metropolitan Railway Stations.

For details of the Classes apply at the Office of the Institute, or by
 letter to the PRINCIPAL.

W. H. DAVISON, M.A.,
 Clerk to the Governing Body.

JUST PUBLISHED. 8vo. 2s. net.

THE
**ANALYTICAL CHEMISTRY
 OF URANIUM.**

By HARRY BREARLEY,
 Joint Author of Brearley and Ibbotson's "Analysis of
 Steel-Works Materials"

LONGMANS, GREEN, AND CO.,
 39, PATERNOSTER ROW, LONDON, E.C.

BIRKBECK COLLEGE

(BIRKBECK INSTITUTION),

Breams Buildings, Chancery Lane, E.C.

DAY AND EVENING SCIENCE CLASSES—

CHEMISTRY	..	..	..	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	..	..	..	A. GRIFFITHS, D.Sc.
MATHEMATICS	..	..	..	E. H. SMART, M.A.
BOTANY	..	..	..	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	..	..	..	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	..	..	..	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING	..	..	..	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board,
 Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.

"CHEM. SOC. JOURNAL," 14 years, 1886
 to 1889, with General Index 83—92, Jubilee vol., &c., complete,
 for 3 years.—Rev. Jones, Hill House, Kidlington, Oxford.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2304.

THE THERMO-CHEMISTRY OF THE THEORY OF ELECTROLYTIC DISSOCIATION.*

By JOSEPH W. RICHARDS.

(Concluded from p. 32).

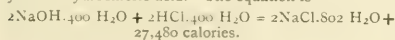
ASSUMING that the heat of formation of salts to dilute solutions represents the heat of formation of the ions from the elements, and further assuming as the basis of calculation the value of the mercury sulphate electrode -0.89 volt, giving the thermo-chemical constant of mercury $-20,500$ calories, we can construct the accompanying table of thermo-chemical constants, which shows the contribution which each base or acid radicle (forming from its elements) furnishes towards the heat of formation of the compound dissolved to dilute solution.

In using these data, the heat of formation of a compound in dilute solution, from its elements, is the sum of the thermochemical constants of its ions, each in dilute solution; the thermochemical constant per chemical equivalent of each ion, however, being multiplied first by the valence of the ion. If the ions, on electrolysis, appear at the electrodes as the elementary constituents of the compound, then the voltage necessary for decomposition is simply the sum of the thermochemical constants of the ions per chemical equivalent divided by $23,040$. If the result of the passage of the current furnishes other products than those at the electrodes, then the heat of formation of these products must be allowed for, and subtracted from the heat of formation of the compound from its elements, in order to find the net work which the current then performs.

It must not be overlooked, either, that the basis or base line on which the table is constructed is an arbitrary one, corresponding to $Hg = Hg' = -41,000$ calories, and that if this value should be really smaller (numerically greater), the thermochemical constants of all bases would be correspondingly decreased, while those of all acid ions would be correspondingly increased, and *vice versa*.

Heat of Neutralisation.

To make immediate and specific application of the principles enunciated in the preceding part of this paper, let us consider the phenomenon of the heat of neutralisation of bases by acids, in dilute solution. Passing at once to a concrete illustration, we will take up Thomson's determination of the neutralisation of dilute caustic soda by dilute hydrochloric acid. The equation is—



The heat of neutralisation per chemical equivalent of the ions concerned is—

$\dagger 13,740$ calories at $18^\circ C$.

In the dilute solution of NaOH we have in the terms of the dissociation theory, ionised molecules of NaOH, viz., Na' and $(OH)'$ ions; or we may make the statement broader, and simply say that we have molecules of NaOH in the condition called "ionised," by the dissociation theorists. From the standpoint of energetics, as explained in the preceding part of this paper, we have in that dilute solution simply combined Na and combined OH, each of these having contributed its thermochemical constant to the heat of formation of the compound. Similarly, in the dilute HCl, we have H' and Cl' ions, or, from the other

standpoint, combined H and combined Cl, forming or constituting the compound HCl.

If these two constituents could be mixed without neutralisation taking place, it will be generally admitted that the solution would contain ions of Na' , $(OH)'$, H' , and Cl' , or, in other words, combined Na, combined (OH) , combined H, and combined Cl. From the standpoint of the dissociation theory, such a solution may equally well be regarded as composed of dissociated NaCl and HOH molecules, as of dissociated NaOH and HCl molecules; similarly, from the standpoint of energetics, it matters not which view we take of such a mixed solution; from this standpoint, it contains simply Na, OH, H, and Cl, all in the combined state.

If we now assume the neutralisation to take place in this mixed solution, what happens? The dissociation theory explains the action very simply by saying that since the resultant solution contains practically only Na and Cl ions, that the H and OH ions have united to form H_2O , and that the heat of neutralisation is the heat of formation of H_2O from H' and $(OH)'$ ions, and is therefore a constant for any acid neutralising any base. To this statement, taken literally, I have very little objection, except to the term "heat of formation of water," as applied to the union of H' and $(OH)'$ to form H_2O .

The term "heat of formation of water" is a thermo-chemical term, implying that the constituents which form the water give up their thermochemical heats of combination and pass from the free state into the state of combination. But no such action, nor even a remotely analogous reaction, takes place when H ions unite with OH ions "to form water." The latter case is not one of thermochemical combination, for the H ions are already in the thermochemically combined state, as HCl, before the act of neutralisation, and the OH ions are similarly already combined as NaOH. It is then a fundamental mistake to regard the neutralisation as proceeding from an act of combination having the least analogy to a chemical act of combination, or of the neutralisation heat having the slightest analogy to thermochemical heat of combination. For, if the H and OH ions have once given out their thermochemical constants, while entering into the state of combination as HCl and NaOH, they cannot give them out again, or any part of them, in any further act of combination. The formation of liquid H_2O from H and OH ions is therefore not a chemical act of combination, and the neutralisation heat is not in any sense thermochemical heat of combination. The heat of neutralisation, therefore, not resulting from chemical combination, must be physical in its nature.

The standpoint of energetics leads to the same view. Whatever the condition of molecules of HCl and NaOH in dilute solution may be, they are still compounds, and their constituents are all in the combined condition. After neutralisation, the Na and Cl are still in the combined condition, as NaCl, and the H and OH are still in the combined condition, as HOH. There has been therefore no change in the condition of any of the constituents named analogous to a change from the free to the combined condition, because they were all in the chemically combined condition before the act of neutralisation and all in the combined state afterwards. The heat evolved in neutralisation would be, therefore, as far as chemical combination occurs, zero, and its source must be a physical one.

The analogy between the molecular condition of a substance in the state of dilute solution, and the molecular condition characteristic of the gaseous state, furnishes the solution of the problem. We do not know exactly what the molecular structure of solids and liquids is, but it is essentially different from that of gases in the property of filling only a fixed maximum space, while gaseous molecules tend to occupy an indefinitely large space. Solid NaOH has a fixed minimum of specific gravity at its melting-point, where the molecules are as far apart as they can get from each other and the mass still retain the con-

* A Paper read at the Fourth General Meeting of the American Electrochemical Society at Niagara Falls, September 19, 1903.

Thermo-chemical Constants of Bases.

		Per formula given.	Per chemical equivalent.
		Calories.	Calories.
Li (solid)	=	Li ⁺ + 62,000	+62,000
K "	=	K ⁺ + 61,000	+61,000
Na "	=	Na ⁺ + 56,300	+56,300
Rb "	=	Rb ⁺ + 61,100	+61,100
N + H ₄ (gases)	=	(NH ₄) ⁺ + 32,500	+32,500
Sr (solid)	=	Sr ⁺⁺ + 115,600	+57,800
Ca "	=	Ca ⁺⁺ + 107,000	+53,500
Mg "	=	Mg ⁺⁺ + 106,800	+53,400
Al "	=	Al ⁺⁺⁺ + 117,600	+39,200
Mn "	=	Mn ⁺⁺ + 48,000	+24,000
Zn "	=	Zn ⁺⁺ + 32,600	+16,300
Fe "	=	Fe ⁺⁺ + 20,000	+10,000
Fe ⁺⁺ (solution)	=	Fe ⁺⁺ - 12,100	-12,100
Cd (solid)	=	Cd ⁺⁺ + 16,200	+ 8,100
Co "	=	Co ⁺⁺ + 14,600	+ 7,300
Ni "	=	Ni ⁺⁺ + 13,600	+ 6,800
Tl "	=	Tl ⁺ + 2,000	+ 1,000
Sn "	=	Sn ⁺⁺ + 2,000	+ 1,000
Pb "	=	Pb ⁺⁺ - 1,000	- 500
H ₂ (gas)	=	2H ⁺ - 1,800	- 900
Cu (solid)	=	Cu ⁺⁺ - 17,600	- 8,800
Pt "	=	Pt ⁺⁺⁺ - 81,400	-20,350
Hg (liquid)	=	Hg ⁺⁺ - 41,000	-20,500
Ag (solid)	=	Ag ⁺ - 26,200	-26,200
Au (solid)	=	Au ⁺⁺⁺ - 93,600	-31,200

Thermo-chemical Constants of Acid Elements.

		Per reaction given.	Per chemical equivalent.
		Calories.	Calories.
O ₂ (gas)	=	2O ⁺ + 86,400	+21,600
Cl ₂ "	=	2Cl ⁺ + 80,600	+40,300
Br ₂ "	=	2Br ⁺ + 66,400	+33,200
I ₂ "	=	2I ⁺ + 28,200	+14,100
F ₂ "	=	2F ⁺ + 107,600	+53,800
S (solid)	=	S ⁺ - 8,400	- 4,200
Se (met.)	=	Se ⁺ - 34,000	-17,000

dition of solid material; liquid NaOH has a fixed minimum of specific gravity, at its boiling-point, where the molecules are as far apart as they can get from each other and the mass still retain the condition of liquid material. If we force the material to occupy a larger space, its molecules pass into the condition characteristic of a gas.

Solution is a process by which the spatial relations of the molecules of the dissolved substance may be indefinitely extended, and by which, therefore, the substance takes on the molecular condition of the gaseous state. A cubic centimetre of solid NaCl dissolved in a cubic metre of water passes as certainly into the gaseous condition as if it had been vapourised, for the molecules of salt are further apart in this dilute solution than they would be in vapour of NaCl. I need scarcely take the time to prove this proposition arithmetically, since this view of the subject is qualitatively and quantitatively proven by the phenomena of osmotic pressure. The facts of osmotic pressure prove that a substance in dilute solution exerts pressure which has all the characteristics of gas pressure, and agrees quantitatively with the pressure which the material could exert in the state of gas if occupying the volume of the solution, but in the gaseous state. The temperature coefficient of the osmotic pressure, moreover, agrees with the gas coefficient. I believe that all will agree, at least, on the very close resemblance or analogy between the gaseous state and the state of being in dilute solution, and a consideration of the heat of neutralisation from the point of view taken in this paper tends to confirm their practical equivalence.

Since the molecule of NaOH in dilute solution exerts osmotic pressure, analogous to its being in the gaseous condition, and the same is true of the molecule of HCl, the two solutions, if mixed without neutralisation taking place, would exert in the mixed condition osmotic pressure as in

each solution separately, all the constituents being in the "ionised" condition and exerting osmotic pressure analogous to gaseous pressure. When neutralisation takes place, only Na and Cl are left in dilute solution, and exert the osmotic pressure, the pressure due to the H and OH has disappeared, coincident with these passing into the condition of liquid water. The act of neutralisation is therefore merely the passage of H and OH from the combined state in dilute solution, in which condition they exert gaseous, osmotic pressure, into the combined state as liquid water, in which they exert practically no osmotic pressure. The change is exactly analogous to the change from the gaseous into the liquid condition, and is therefore the equivalent of the condensation of water vapour into the liquid state. The source of the heat of neutralisation is therefore the physical change of state of HOH from the gaseous to the liquid condition, without any heat of chemical combination being concerned or even possible, because the ingredients, H and OH, are as much in the combined condition before the act of neutralisation as after it.

To verify this statement quantitatively, we need to take into consideration the fact that 2NaOH.400H₂O will occupy 7.2 litres (if the molecular weights be expressed in grammes), and the NaOH will exert an osmotic pressure of 12.34 atmospheres. The 2HCl.400H₂O occupies an equal volume, and the HCl exerts a similar osmotic pressure. After the mixing of the solutions the osmotic pressure exerted by each molecule in solution is halved, but the total osmotic pressure is 12.34 atmospheres. After neutralisation, there remains only the osmotic pressure of the 2NaCl in the 802H₂O, which is 6.15 atmospheres, the osmotic pressure of the H and OH together equal to 6.19 atmospheres, disappearing because of the condensation of the water to the liquid state. The heat given out in

Thermo-chemical Constants of Acid Radicals.

		Per reaction given.	Per chemical equivalent.	Salt formed.
		Calories.	Calories.	
O ₂ (gas) plus H ₂ (gas) equals	2(OH)'	+ 112,200	+ 56,100	Hydrate.
S ₂ (solid) " H ₂ " "	2(SH)'	+ 8,000	+ 4,000	Sulphydrate.
Se ₂ (met.) " H ₂ " "	2(SeH)'	+ 40,000	+ 20,000	Selenhydrate.
Cl ₂ (gas) " O ₂ " "	2(ClO)'	+ 56,800	+ 28,400	Hypochlorite.
Cl ₂ " " 3O ₂ " "	2(ClO ₂)'	+ 45,600	+ 22,800	Chlorate.
Cl ₂ " " 4O ₂ " "	2(ClO ₃)'	+ 80,600	+ 40,300	Perchlorate.
Br ₂ " " O ₂ " "	2(BrO)'	+ 59,000	+ 29,500	Hypobromite.
Br ₂ " " 3O ₂ " "	2(BrO ₂)'	+ 20,800	+ 10,400	Bromate.
I ₂ " " 3O ₂ " "	2(IO)'	+ 131,800	+ 65,900	Iodate.
I ₂ " " 4O ₂ " "	2(IO ₂)'	+ 107,000	+ 53,500	Periodate.
4S (solid) " 3O ₂ " "	2(S ₂ O ₃)'	+ 290,600	+ 72,650	Hyposulphite.
2S " " 3O ₂ " "	2(SO ₃)'	+ 304,000	+ 76,000	Sulphite.
2S (solid) + 3O ₂ (gas) " H ₂ " "	2(HSO ₃)'	+ 300,600	+ 150,300	Bisulphite.
4S (solid) " 5O ₂ " "	2(S ₂ O ₅)'	+ 404,400	+ 116,100	Pyrosulphite.
S " " 2O ₂ " "	(SO ₃)'	+ 215,800	+ 107,900	Sulphate.
H ₂ (gas) + 2S " " 4O ₂ " "	2(HSO ₄)'	+ 424,400	+ 212,000	Bisulphate.
2S " " 4O ₂ " "	(S ₂ O ₈)'	+ 318,000	+ 159,000	Pyrosulphate.
3S " " 3O ₂ " "	(S ₃ O ₆)'	+ 278,500	+ 139,250	Dithionate.
3S " " 3O ₂ " "	(S ₃ O ₆)'	+ 274,800	+ 137,400	Trithionate.
4S " " 3O ₂ " "	(S ₄ O ₆)'	+ 263,000	+ 131,500	Tetrathionate.
5S " " 3O ₂ " "	(S ₅ O ₆)'	+ 268,000	+ 134,000	Pentathionate.
2Se " " 3O ₂ " "	2(SeO ₃)'	+ 243,800	+ 60,950	Selenite.
Se " " 2O ₂ " "	(SeO ₄)'	+ 147,400	+ 73,700	Selenate.
N ₂ (gas) " O ₂ " "	2(NO)'	- 5,800	- 2,900	Hyponitrite.
N ₂ " " 2O ₂ " "	2(NO ₂)'	+ 55,800	+ 27,900	Nitrite.
N ₂ " " 3O ₂ " "	2(NO ₃)'	+ 99,400	+ 49,700	Nitrate.
P (solid) " 2O ₂ " "	(PO ₄)'	+ 300,600	+ 100,200	Phosphate.
H ₂ (gas) + 2P " " 4O ₂ " "	2(HPO ₄)'	+ 614,600	+ 153,650	Mono-H-phosphate.
H ₂ (gas) + P " " 2O ₂ " "	(H ₂ PO ₄)'	+ 308,600	+ 308,600	Di-H-phosphate.
As " " O ₂ " "	(AsO ₂)'	+ 206,100	+ 103,050	Arsenite.
As " " 2O ₂ " "	(AsO ₄)'	+ 213,300	+ 71,100	Arsenate.
H ₂ (gas) + 2As " " 4O ₂ " "	2(HAsO ₄)'	+ 435,800	+ 72,600	Mono-H-arsenate.
H ₂ (gas) + As " " 2O ₂ " "	(H ₂ AsO ₄)'	+ 218,100	+ 218,100	Di-H-arsenate.
2C (amorph.) " N ₂ " "	2(CN)'	- 68,000	- 34,000	Cyanide.
O ₂ (gas) + 2C " " N ₂ " "	2(CNO)'	+ 76,000	+ 38,000	Cyanate.
2S (solid) + 6C " " N ₂ " "	2(CNS)'	- 34,400	- 17,200	Thiocyanate.
Fe (solid) + 6C " " 3N ₂ " "	(FeC ₆ N ₆)'	- 98,800	- 24,700	Ferrocyanide.
Fe (solid) + 6C " " 3N ₂ " "	(FeC ₆ N ₆)'	- 155,800	- 51,900	Ferricyanide.
2C " " 3O ₂ " "	2(CO ₃)'	+ 333,400	+ 83,350	Carbonate.
H ₂ (gas) + 2C " " 3O ₂ " "	2(HCO ₃)'	+ 340,000	+ 170,000	Bicarbonate.
H ₂ (gas) + 2C " " 2O ₂ " "	2(CHO ₂)'	+ 211,000	+ 105,500	Formate.
3H ₂ (gas) + 4C " " 2O ₂ " "	2(C ₂ H ₃ O ₂)'	+ 242,800	+ 121,400	Acetate.
2C " " 2O ₂ " "	(C ₂ O ₄)'	+ 201,400	+ 100,700	Oxalate.

this condensation is equal numerically to that necessary to convert 2H₂O in the liquid state into vapour exerting in the gaseous state a pressure of 6·19 atmospheres.

The latent heat of vapourisation of 1 kilo. of H₂O at 0° is 606·5 calories (Regnault), or for 18 parts 10·917 calories. If we subtract the outer work done in giving tension to the vapour (2T) the work of vapourisation without outer work is 10·917 - 546 = 10·371 calories. At 18° by a similar calculation the work of vapourisation is—

$$(594 \times 18) - 2(273 + 18) = 10,692 - 582 = 10,110 \text{ calories.}$$

The outer work, however, if the vapour exerts 6·19 atmospheres pressure, is 6·19 × 2T = 6·19 × 582 = 3590 calories. The total work of vapourisation, including the work necessary to give the vapour the requisite tension of 6·19 atmospheres is 10,110 + 3590 = 13,700 calories. Therefore, combined H and OH, at a tension of 6·19 atmospheres, will give out in condensing to combined H and OH, as liquid water, at 18° C., 13,700 calories. The heat of neutralisation, 13,740 calories, is, therefore, nothing else than the physical heat of condensation of 18 parts of combined H and OH to 18 parts of liquid water.

An exactly similar conclusion follows from a thermo-chemical consideration of the heat of formation of an "ionised" H₂O molecule in dilute solution. The thermochemical constants of H· and (OH) are already given in the tables, and their sum must be the heat of formation of water from hydrogen and oxygen gases,

when the molecule remains in dilute solution, i.e., "ionised."

$$\begin{aligned} \text{H} \cdot &= -900 \text{ calories} \\ (\text{OH})' &= +56,100 \text{ " } \\ \text{Sum} &= +55,200 \text{ " } \end{aligned}$$

This represents the heat of formation in dilute solution, with the molecule "ionised," so as to exert the usual osmotic pressures of H and OH ions in the dilute solutions used. In the concrete case of mixed NaOH and HCl solutions, we have found this osmotic pressure to have been 6·17 atmospheres. To calculate what the heat of formation of the "ionised" molecule would be if it exerted 1 atmosphere pressure, we add to 55,200 the work of expansion from 6·19 atmospheres to 1 atmosphere = 6·19 - 1 × 2T = 5·19 × 582 = 3021 calories, giving a total of 58,221 calories. But the heat of formation of vapour of water at 18° from oxygen and hydrogen gas, as nearly as can be calculated from Regnault's experiments, 88,100 calories. It thence follows, that the heat of combination of hydrogen and oxygen gases to form an "ionised" molecule, in dilute solution, the ionised molecule exerting an osmotic pressure of one atmosphere, is equal to or identical with the heat of combination to form vapour of water at one atmosphere tension; from which follows the substantial identification of the "ionised" water molecule H· and (OH)' ions at a

given osmotic pressure) with the gaseous state of water vapour at the same pressure.

Two lines of reasoning and calculation therefore give proof to the thesis, that the heat of neutralisation is merely the heat evolved in the condensation of a gaseous H_2O molecule into the liquid state, and this conclusion, again, agrees further with the conception that the "ionised" condition of a molecule in dilute solution is merely a certain physical condition of the compound, and that "ionisation" is in no sense to be regarded as a resolution or decomposition of the molecule into its constituents. An "ionised" molecule is still a molecule of the compound, with its constituents still in the combined condition.

If it be objected that the heat of neutralisation is not a constant for all acids and bases, but that there are irregularities, it has been shown by Arrhenius that these irregularities are due to imperfect or incomplete "ionisation" of either the acid or base or both, and that when this is allowed for, the irregularities disappear or are explained. Exactly the same line of reasoning would account for the irregularities, assuming the line of explanation of the heat of neutralisation which has been brought forward in this paper.

Metallurgical Laboratory,
Lehigh University.

A PROPOSED METHOD OF TESTING WOOD TREATED TO RESIST FIRE.*

By CHAS. F. McKENNA

(Concluded from p. 33).

THE following experiments demonstrate that the gas yield and coal from the distillation of small pieces of some of the more common woods could be used as a criterion of the extent of retardation of fire caused by the proofing processes.

Spruce; 0.500 grm.; fireproof; heated for two minutes by 9 ampere current:—

Gas yield		116.5 c.c.
" "		124.5
" "		117.0
Average		119.3

The same wood leached in boiling water and dried to normal moisture:—

Gas yield		136.5 c.c.
" "		129.0
" "		136.0
Average		133.8

Birch; 0.500 grm.; 8 ampere current for two minutes:—

Gas Yield.		
Untreated.		Treated
164 c.c.		151 c.c.
165		160
171		162
163		153
167		
Average ..	166.4	156.5

The four specimens of char of the treated wood showed an average weight of 147.6 mg., and those of the untreated wood averaged 100 mg. The percentage of charcoal left in the treated wood was 29.5 per cent, and in the other 20 per cent.

With exercise of more care, similar experiments gave the following results:—

Birch; 0.500 grm.; 7 ampere current, 125 volts, two minutes:—

Gas Yield.		
Untreated.		Treated.
125 c.c.		95 c.c.
127		105
124		105
126		103
126		108
132		104
Average ..	126.6	103.3
Charcoal.		
Untreated.		Treated.
0.1037 gr.		0.1643 gr.
0.1026		0.1540
0.1065		0.1595
0.1025		0.1700
0.1062		0.1681
0.1016		0.1661
Average ..	0.103541	0.16366

The following experiment was performed with the assistance of one of the companies practising the fire-proofing art: A sample of birch, of which I was given an initial untreated specimen, was fireproofed for me in a small test cylinder, using a solution of the density with which they were accustomed to operate on a large scale. Two solutions of less density by one-third and two-thirds of the dissolved salts were also prepared and used on specimens of the same wood on separate runs of the cylinder. I was thus provided with four specimens of wood of the same lot: the first, natural; the second, treated with a dilute solution; the third, with one more dense; and the fourth, with once most dense. These were numbered "0," "1," "2," and "3," respectively. In the test retort they gave the following results:—

0.500 grm.; 7 ampere current, 125 volts, two minutes:—

Gas Yield.			
"0"	"1"	"2"	"3"
112 c.c.	89 c.c.	99 c.c.	97 c.c.
108	92	97	95
104	88	92	92
107	87	99	93
107	89	95	91
Average 107.6	88.6	96.4	93.6

Average weight of the charcoal from each:—

	Milligrams	Per cent
"0"	103	20.6
"1"	130	27.2
"2"	120	24.0
"3"	133	26.6

If the decomposition into gaseous products and coal measures the value of the treatment, the least dense solution gave the best result, which is probably true, as it was an alum process, and the penetration of the cell walls was probably more perfect with the most dilute solution.

Experiments with Yellow Pine, treated by another process and patent than the preceding. This yellow pine gave the following results (as there was no original stock offered, the "untreated" specimens were obtained from scraps of yellow pine in a carpenter shop):—

0.500 grm.; 8 ampere current, 125 volts, two minutes:—

Gas Yield.		
Untreated.		Treated.
125 c.c.		87 c.c.
131		86
128		88
133		86
134		86
Average ..	130.2	86.6

Average weight of four samples of charcoal :

Untreated . . . 0.0179 grm. or 19.58 per cent.
Treated . . . 0.0192 grm. or 38.24 per cent.

Yellow pine untreated:—

(a) Dried.

(b) With normal moisture, 7.1 per cent more water than (a).

Gas Yield.

(a)	(b)
139 c.c.	128 c.c.
136	132
143	134

Average . . 136

Charcoal, average weight:—

(a)	(b)
0.102 grm.	0.0963 grm.

Yellow pine, treated:—

(a) Dried.

(d) With normal moisture, 3.6 per cent more water than (a).

Gas Yield.

(a)	(b)
90 c.c.	92 c.c.
91	88
89	88
90	85

Average . . 90

Charcoal, average weight:

(a)	(b)
0.198 grm.	0.1882 grm.

Three questions arise:—Will not errors be introduced by the moisture of the wood? This is to be met in the same way as in previous methods of test; namely, by the preparation of dried samples subsequently exposed for the absorption of the normal amount of water. Whether it would vitiate the results obtained by inspectors having limited facilities for such work will have to be determined. Are not the results modified by the superior density of the treated sample over the normal wood that contains no salts? Naturally this should be so in finding the weight of the char residue; but in all experiments it seems to be an unimportant quantity, and in some it would appear that the wood which is heavier from treatment with the dense solution of an inferior fire-proofing salt will give a very large gas yield. Would not gases generated from the chemicals also modify the results? The only process where it possibly would be in using ammonium salts or carbonates, and proper provision should be made for the absorption of the gases as each case would require.

It would seem to me to be indicated by the preceding that the degree to which total decomposition without air can be inhibited by previous chemical treatment in wood subjected to a high heat can be definitely measured by subjecting small test pieces to distillation, that this test operation can be easily, quickly, and accurately performed in the small retort as shown, and that the number of such tests which can be made in a short time on small pieces is so great that a good average could be selected in chips from different parts, interior, exterior, &c., of lots of timber as delivered. It seems probable also that in the conditions surrounding experiments in such a retort, an equally accurate measure can be found of the resistance to inflammation of woods before and after treatment, with access of air.

I hope to continue such experiments in the future, if circumstances favour.

REPORT ON ASH.*

By G. S. FRAPS.

BEFORE sending out samples or requests for co-operation the referee undertook the following work on the determination of sulphur:—

PRELIMINARY WORK ON SULPHUR.

The following methods were studied:—

1. Nitric-acid Method (the Provisional Method of the Association).

Five grms. of material are placed in a 3½-inch porcelain evaporating dish, 20 c.c. of nitric acid (concentrated) added, and the mixture heated cautiously on the water-bath until all danger of overflowing has passed. It is then partly evaporated, 10 c.c. of a 5 per cent solution of potassium nitrate is added, the mixture evaporated to complete dryness, and ignited, at first gently, then under a blast-lamp until the residue is white. It is then dissolved in hydrochloric acid, evaporated to dryness, and heated for some time in an air-bath to render silica insoluble. The residue is taken up in water with the addition of a little acid, filtered, and the sulphuric acid precipitated with barium chloride in the usual way.

This method gives good results. It has a disadvantage, however, in that the ash produced is easily fusible, acts upon the porcelain dish, and is ignited free of carbon with great difficulty. It was to overcome this objection that the modification described below was tested.

2. Nitric Acid Method Modified.

The modification consists in the use of 20 c.c. of a solution of calcium acetate containing 0.56 grm. of calcium oxide (CaO), in place of 20 c.c. of potassium nitrate solution. The ignition takes place much more easily, the ash does not fuse, and is more easily burned free of carbon than when potassium nitrate is used.

3. Boiling with Nitric Acid.

An attempt was made to destroy the organic matter by boiling the material with nitric acid, which I understand is the method used for meats in the nutrition investigations of the Office of Experiment Stations. The method did not succeed with vegetable materials. Several experiments were made, but in no case was all organic matter of the vegetable materials destroyed, even when 5 grms. of material was boiled to dryness with 100 c.c. nitric acid in a Kjeldahl flask. As it would therefore be necessary to wash the residue from the flask into a dish, and ignite with the addition of potassium nitrate or calcium acetate to remove organic matter, this method would differ from the two preceding only in that a larger quantity of acid is used and the digestion with the acid is more prolonged. The method was not further examined.

4. Fusion with Caustic Soda.

This is the standard method for determining sulphur in non-volatile organic compounds. The method as tested was as follows:—

Five grms. of material in a nickel crucible were saturated with 40 c.c. of a solution of 150 grms. sodium hydroxide in 300 c.c. water, evaporated to dryness, and fused with the addition of a little sodium peroxide. The fusion requires care to prevent the material from overflowing the dish, and the whole process is somewhat long. The melt was dissolved in water, neutralised, and acidified with hydrochloric acid, evaporated to dryness, and heated to render silica insoluble, filtered, and the sulphuric acid precipitated from the filtrate, the volume of which was about 200 c.c. The sodium hydroxide and sodium peroxide contained a large quantity of sulphates; about 0.1 grm. in the quantity used in the determination was found in the blank determination.

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

The results with this method are decidedly low. This may possibly be due to the solubility of barium sulphate in sodium chloride, about 38 grms. of the latter salt being present in the solution from which the barium sulphate was precipitated, or it may be owing to the error caused by impurities in the reagents.

5. Eschka's Method.

This is the method usually employed for the determination of sulphur in coals. It was applied to plant materials as follows:—

Five grms. material were intimately mixed in a platinum dish, with 7½ grms. of a mixture of two parts magnesium oxide to one of dried sodium carbonate. The mixture was heated, stirring frequently, and the temperature raised slowly until all carbon appeared to be burned off. The mass was transferred to a beaker with about 50 c.c. water; 15 c.c. of saturated bromine water was added, and boiled five minutes. It was allowed to settle, decanted through a filter, boiled a second and third time with about 30 c.c. water, and washed thoroughly. The filtrate was made acid with hydrochloric acid, boiled until bromine was expelled, and then precipitated with barium chloride in the usual way. The results by this method were too low.

Results of Work.

The analytical results by the different methods are given in the following table (Table I.). The figures in each case are corrected for the sulphur in the reagents found by a blank determination. The blank was very low in the case of the two nitric acid methods. In the Eschka method it was equivalent to 0.0058 grm. barium sulphate in the quantity of the reagents used for each test. As has already been stated, the fusion method gave results much too low, and the blank was high, being 0.1103 grm. barium sulphate.

TABLE I.—Determination of Sulphur (SO₃) by Different Methods.

	Nitric acid method.	Nitric acid modified.	Eschka method.
	Per cent.	Per cent.	Per cent.
Corn	0.249 0.244	0.287 0.286	0.238 0.208
Average ..	0.247	0.287	0.223
Peas	0.481 0.533 0.503	0.480 — —	0.297 0.312 0.313
Average ..	0.518	0.480	0.307
Millet	0.369 0.376 0.400	0.427 0.434 —	0.451 0.460 —
Average ..	0.382	0.431	0.456

Official Work on Sulphur.

It was decided to compare the provisional method for the determination of sulphur with the method modified by the use of calcium acetate in place of potassium nitrate. A comparison between two methods for potash was also determined. The following circular letter was sent out to a number of members of this body:—

Raleigh, N.C., May 1, 1902.

DEAR SIR,—The referee on ash for the present year will continue the study of the methods of determining sulphur and potash in plant materials. It is thought best to work out one portion of the problem at a time. Kindly inform the referee if you will be able to co-operate. The samples will be sent out about the latter part of May. The work of last year proves conclusively that the sulphur in an ash, as ordinarily prepared, is no indication of the amount of sulphur in the plant, which

may be vastly greater. Kindly give us the benefit of any suggestions.—Very truly,

G. S. FRAPS, Referee.

FRANK T. SHUTT, Associate Referee.

Eight chemists requested samples. R. J. Davidson, of Virginia, sent the following table of analyses:—

TABLE II.—Determination of Sulphur (SO₃) by Different Methods (Davidson).

Method.	Dried apples, sample 1.	Dried apples, sample 2.	Bran.
	Per cent.	Per cent.	Per cent.
Ignition with calcium acetate	0.09	0.10	0.27
Nitric acid method	0.09	0.10	0.45
Eschka's method	0.10	0.11	—
In ash	—	—	0.09

W. P. Headen, of Fort Collins, Colo., wrote as follows:—

If you will refer to my Bulletin on Alfalfa, No. 35, of this station, pages 84–87, you will see that I did some work in this line in 1895 in regard to chlorine, sulphur, and phosphorus, but did nothing in regard to loss of potash. I found a very considerable loss of chlorine and sulphur, but none for phosphoric acid. I was rather surprised at the latter, as we know that phosphates heated with carbon, especially if there is sand enough present to set phosphoric acid free, may be reduced. In my experiments there were doubtless enough basic salts present to avoid such reactions; besides, the temperature of incineration was very low—as low as would accomplish the incineration.

You state that the sulphur in the plant may be vastly greater than that indicated by the determination of sulphuric acid or total sulphur in the ash. You will see that I found in one instance 4.88 per cent in the ash and 8.09 per cent in the plant, almost 66 per cent more.

Mr. Charles P. Beistle wrote as follows:—

I would say that I have done considerable work on the determination of sulphur in plant substances and proteid bodies, and have found the only satisfactory way is by fusion in a mixture of sodium hydrate and potassium nitrate. Among other methods used were ignition in a closed vessel containing oxygen under about 20 atmospheres pressure, ignition in a combustion tube in a current of oxygen gas, passing products of combustion through bromine water, and digestion in nitro-hydrochloric acid. The first mentioned method always gave the highest results. The next two methods gave almost as high results, but required special apparatus and a great expenditure of time. To determine sulphur in the ash of plants gives no indication whatever of the amount of sulphur present in the original material, and the calcium acetate method (simple ignition with calcium acetate), although giving higher results, is of no real value as a method of estimating total sulphur.

I would suggest that fusion with sodium peroxide might be successfully used as a method of oxidising the plant material and changing sulphur to sulphate.

Work on Ash.

Two samples were prepared, corn bran and cotton-seed meal, and sent out with the following letter:—

Directions for Work.

The samples consist of corn bran and cotton-seed meal. Determine moisture (in the usual way), sulphur, and potash in both samples. Make at least two determinations by each method. In reporting give weights of precipitates, per cent on samples as received, and on dry matter. Please report results as early as possible.

METHOD I.—Sulphur.

Place 5 grms. material in a 2½-inch porcelain evaporating dish, add 20 c.c. concentrated nitric acid, and heat the mixture cautiously on the water-bath until all danger of overflowing has passed. Then evaporate partly, add 10 c.c. of 5 per cent solution of potassium nitrate, evaporate to complete

dryness, and ignite, at first gently, then more vigorously until the residue is white. The residue is then dissolved in hydrochloric acid, evaporate to dryness, and heated for some time in an air-bath to render silica insoluble. The residue is taken up in water with the addition of a little hydrochloric acid, filtered to 150 c.c. or more, and the sulphuric acid precipitated with barium chloride in the usual way. Make a blank test with the reagents.

METHOD II.—Sulphur.

The same as the preceding, substituting 20 c.c. of a solution of calcium acetate for the potassium nitrate. The solution is prepared by dissolving 12.5 grms. calcium carbonate, chemically pure, in chemically pure acetic acid, and diluting to 250 c.c. Make a blank test with the reagents.

METHOD III.—Potash.

Determine by ignition with sulphuric acid as in the methods of the Association of Official Agricultural Chemists, page 22b. With the bran use a quantity of the solution corresponding to at least 2 grms. of bran.

METHOD IV.—Potash.

Char 10 grms. substance in a platinum dish, extract twice with hot dilute hydrochloric acid 1:10, and wash, receiving the extract and washing in a 500 c.c. flask. Return filter and contents to the dish, and ignite to whiteness. Dissolve the residue in hydrochloric acid, add to the extract in the flask, make up to volume, and determine potash as in Method III.

Report potash as K_2O , sulphur as SO_3 . Please give the referee the benefit of your suggestions in regard to the work.

Moisture.

The moisture determinations on the samples sent out are given simply as a matter of record (Table III.). The agreement is satisfactory.

TABLE III.—Moisture Determinations.

Analyst.	Corn bran.		Cotton-seed meal.	
	Per cent.	Per cent.	Per cent.	Per cent.
J. H. Gibboney, Virginia	12.10	7.28		
E. G. Runyan, Washington D.C. ..	12.67	7.20		
Frank T. Shutt, Ottawa	12.30	6.97		
A. T. Charron, Ottawa	12.55	7.08		
R. W. Thatcher, Washington ..	13.02	7.96		
	13.07	8.01		

Determination of Sulphur (SO_3).

The results obtained for sulphur in the samples as sent out are given in the following table:—

TABLE IV.—Determination of Sulphur (SO_3).

Analyst.	Corn bran.		Cotton-seed meal.	
	Pro- visional method.	Modified provisional method.	Pro- visional method.	Modified provisional method.
	Per cent.	Per cent.	Per cent.	Per cent.
J. H. Gibboney, Virginia	0.27	0.32	1.06	1.07
	0.28	0.34	1.07	1.10
	0.28	0.30	1.01	1.00
E. G. Runyan, Wash- ington, D.C.	0.43	0.33	1.04	1.08
	0.42	0.34	1.05	1.08
	0.44	0.32	1.04	1.14
Frank T. Shutt, Ottawa	0.40	0.15	1.27	1.10
	0.40	0.13	—	1.05
A. T. Charron, Ottawa	0.34	0.24	1.24	1.00
	0.34	0.24	1.34	1.08
G. S. Fraps, North Carolina	—	0.41	—	1.03
	—	0.40	—	1.00
	—	—	—	1.03
	—	—	—	1.08
R. W. Thatcher, Wash- ington	0.27	0.24	0.99	0.97
	0.23	0.25	1.00	0.97

Remarks of Analysts.

R. J. Davidson, Virginia.—We tried several determinations on these substances by Eschka's method, but found the result too low. On 2 grm. samples we got the following weights of barium sulphate: 0.0240, 0.216, and 0.0200 grm. just about one-third of what they should be.

R. W. Thatcher, Washington.—My experience with the two methods suggested for the determination of sulphur is that they give practically identical results, those obtained by the calcium acetate ignition method being very slightly lower. The use of calcium acetate allows much more rapid burning to whiteness, since the potassium nitrate present in the other method fuses very easily, and thus encloses particles of carbonaceous matter, which are finally removed only after a somewhat tedious process.

Frank T. Shutt, Central Experimental Farm, Ottawa, Canada.—We found great difficulty in obtaining a white ash by Method II. Even after prolonged ignition the ash remained grey, and on treatment with acid showed the presence of carbon. You will notice that invariably higher results were obtained by Method I. As far as one can judge from duplicate determinations and general conduct and appearance of the material during treatment, Method I. seems to be very satisfactory. To lessen the danger from loss while frothing (treatment with nitric acid on water-bath) a 3-inch porcelain evaporating dish was used. It will be found much safer than a 2½-inch dish. Ignition in a muffle furnace proved easier and quicker than with the blast-lamp.

The agreement between the figures obtained by different analysts by both methods is not satisfactory. The trouble is with the methods. They are not very accurate. As will be shown below, the results given by the nitric acid method are much lower than they should be.

(To be continued.)

PRECIPITATION AND SEPARATION BY WEAK ORGANIC BASES.*

By E. T. ALLEN.

A LARGE number of organic bases are known, which may serve as quantitative precipitants of many metallic hydroxides, though they usually present no advantage over ammonia or the fixed alkalis. Of late, more especially (*Journ. Am. Chem. Soc.*, xxiv., 540, and xxi., 776), some of them have found use for analytical separations, where the inorganic reagents are not applicable. We have, between the organic and inorganic bases, a nearly complete analogy. The tetrammonium compounds are well known to be highly dissociated in aqueous solution, giving, in a marked degree, the characteristic hydroxyl reactions, like the hydroxides of the alkalis and thallium. A second weaker class of bases comparable, in general, with ammonia are the paraffin amines. These also are strongly alkaline in reaction, and capable of precipitating all but the strongest metallic bases, whose solubility products are too high to be reached by such concentrations of hydroxyl as these reagents afford.

A third class of bases in which the aromatic amines, quinoline, naphthylamine, phenylhydrazine, &c., may be named, have no soluble analogues in the inorganic field, though they are akin to the bases formed by the metals of the third and fourth groups of the periodic system.

With indicators they give either a faint alkaline reaction or none at all. When a metallic salt is precipitated by such a base, say aniline, the solution remains acid even when a considerable excess of the reagent has been added. It is plain, therefore, that only those bases which can be thrown down in acid solution, can be precipitated here. All chemists are familiar with the precipitation of certain hydroxides by the action of water alone. Such reactions

* From the *Journal of the American Chemical Society*, xxv., No. 4.

are always reversible. We may instance the case of titanium sulphate, $\text{Ti}(\text{SO}_4)_2 + 4\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{Ti}(\text{OH})_4$.*

The complete precipitation of the titanium evidently depends on the reduction of the concentration of free acid to a point where the titanium hydroxide is no longer appreciably soluble. Let us suppose the precipitation to be incomplete. If now we should add to the system a weak base like aniline, a certain quantity of the free acid would be converted into neutral salt, and thus the concentration of the acid would be diminished, though an appreciable quantity would always remain unless a very great excess of reagent were used, for, according to the principles of hydrolysis, the salt of a weak base must be partially decomposed by water into free base and free acid. Thus, $\text{C}_6\text{H}_5\text{NH}_2 + \text{HCl} = \text{C}_6\text{H}_5\text{NH}_3^+ \text{Cl}^-$.

The precipitation of titanium will therefore go further, in fact, to completion when a proper quantity of aniline has been added, because in small concentrations of acid, titanium hydroxide is practically insoluble. The degree of the hydrolysis of the aniline hydrochloride is conditioned by temperature, by the degree of dilution, and by excess of free base. Speaking in general of this class of weak bases, it is, of course, true that the degree of hydrolysis, in other words the concentration of free acid in solutions of their salts, depends on the strength of the base. Some organic bases are so weak that they would doubtless be of no service for any quantitative precipitation, but those whose hydrochlorides are hydrolysed to an extent of several per cent in dilute solutions form a group well adapted for the separation of weak from strong metallic bases. For the strong bases like magnesia, the alkaline earths, &c., are incapable of existence with free acid, while the weak ones, whose salts are more or less hydrolysed in aqueous solution, are practically insoluble in such concentrations of acid as one can readily obtain by the above means. This is the principle of most analytical separations by weak organic bases, and the most important one involved in the experimental part of this paper. Of course there are cases in which the precipitate by an organic base re-dissolves in excess. Thus several paraffin amines re-dissolve the hydroxides of aluminium, copper, silver, zinc, &c., and it is possible some of the weaker bases may yield separations on this principle, though no cases of the kind are known to me.†

In the study of the separations in the sequel, it seemed of interest, not merely to determine the necessary empirical conditions, but also to inquire how much acid is freed from the salts of certain weak bases—the precipitants—under definite conditions of dilution, temperature, and excess of the base. Thus the hydrolytic constant,—

$$K = \frac{\text{BOH} \times \text{HCl}}{\text{V}(\text{BCl})}$$

of aniline and of phenylhydrazine hydrochloride was determined in N/10 solutions at a temperature of 40° C. In this way could be made an approximation to the concentration in free acid possessed by the solutions in which the separations were made—concentrations in which certain weak metallic bases remain without dissolving appreciably.

Separation of Aluminium from Iron.

Several years ago Campbell and Hess (*Journ. Am. Chem. Soc.*, xxi., 776) described a method for precipitating aluminium in the presence of iron after the latter had been reduced to the ferrous state by sulphurous acid. The reagent used was phenylhydrazine. The results appeared satisfactory, and, as a good method for the direct determination of aluminium in the presence of iron was needed, Dr. W. F. Hillebrand suggested that I study this separation more closely, especially in regard to its application to rock analysis, where titanium is nearly always present, and sometimes zirconium. I desire in this place to express to Dr. Hillebrand my best thanks for this suggestion.

* The principle involved is the same whether the precipitate be a hydroxide or a basic salt.

† In his statement that phenylhydrazine throws down, from thorium nitrate, a "canary-yellow precipitate, easily soluble in excess," Miss Jefferson appears to be in error (*Journ. Am. Chem. Soc.*, xxiv., 546).

In brief, my results indicate that it is practically impossible to separate the iron completely in one precipitation. With a double precipitation the results are good. When the quantity of precipitated alumina is large, there is apt to be a loss, which I ascribe to the long contact with the faintly acid wash solution which is necessary to remove the iron. Thus I have obtained on certain rocks results which were considerably lower than those carefully determined by difference in the usual way. On the other hand, from mixtures of iron, aluminium, titanium, and zirconium salts made up from standard solutions the results have been satisfactory. This discrepancy has not thus far been explained. The method is excellently adapted to the separation of very small quantities of aluminium, such as a milligram, or even less, from a large excess of iron, a point of considerable practical importance.

In the following tests, standard solutions of ferric and aluminium chlorides were used. The former was prepared from piano wire by dissolving in pure hydrochloric acid, filtering, oxidising with chlorine, and driving out the excess from the hot solution by a current of air. No alumina or other bases of similar strength could be detected in this solution. It was standardised by precipitation with ammonia. The aluminium chloride was prepared by dissolving "C. P." metal in hydrochloric acid, filtering off the silicon, and diluting. The exact strength was determined by precipitation with ammonia. The solution contained only a trace of iron.

To the conditions laid down by Campbell and Hess a few additions might be made. The volume of the solution may vary, according to the quantity of alumina to be precipitated, from 100 to 200 c.c. It should be heated and reduced by adding saturated ammonium bisulphite. From 5 to 20 drops, according to the quantity of iron, may be used. If the solution turns deep red (ferric sulphite) it is not acid enough, and a few drops of hydrochloric acid should be added, for the sulphite itself does not reduce ferric salts, at least not with rapidity. Now quickly bring to neutrality with ammonia, and then add several drops of dilute hydrochloric acid. If this last operation is done too slowly, the oxygen of the air helps to form a little ferric hydroxide which does not always readily dissolve in the dilute acid. Finally, add from 1 to 3 c.c. phenylhydrazine,* according to the weight of the alumina to be precipitated. If too little has been used, a few drops added to the filtrate will disclose the mistake. Stir until the precipitate has become sufficiently flaky, and allow to settle. The supernatant liquid will now be plainly acid to litmus. One need not be disturbed if the precipitate has a brownish colour, for it is not due to ferric hydroxide, but to the colouring matter contained by all phenylhydrazine which has not been freshly distilled. When the determinations are allowed to stand too long, the air increases this oxidation product, and a brown insoluble scum forms on the surface of the liquid and on the sides of the vessel, which is rather troublesome to the analyst. Fortunately equilibrium appears to be established in a short time. The vessels need not stand more than an hour at any rate.†

Precipitation of Alumina alone by Phenylhydrazine.

1 c.c. $\text{AlCl}_3 = 0.00500$ grm. Al_2O_3 .			
	Found.	Grm.	Error.
	Taken.	Grm.	Grm.
I	50 c.c. = 0.2500 grm. Al_2O_3	0.2487	-0.0013
	25 c.c. = 0.1250 grm. Al_2O_3	0.1236	-0.0014
	5 c.c. = 0.0250 grm. Al_2O_3	0.0254	+0.0004

The tendency toward low results is here plainly visible.

(To be continued).

* The reagent should, of course, be free from inorganic impurities which could disturb the results. The author found one sample, which, after persistently giving high results, was proved to contain tin, which had probably been used in its preparation.

† The precipitate is washed by a solution of phenylhydrazine sulphite, made by adding cold saturated sulphurous acid to a little phenylhydrazine until the crystalline sulphite first formed dissolves in the excess. The solution has an acid reaction. Five to 10 c.c. of this are used in 100 c.c. hot water. See Campbell and Hess, *loc. cit.*

THE ANALYSIS OF COMMERCIAL NICKEL.

By A. HOLLARD.

Impurities.—Copper, cobalt, iron, alumina, lime, magnesia, sulphur, silica, carbon, arsenic, antimony.

Estimation of the Nickel.—5 grms. of the metal are placed in a Bohemian beaker 65 m.m. diameter and 180 m.m. in height. It is in this same glass that the attack of the metal, the evaporation, and its subsequent electrolysis will be successively carried out. The great height of the glass is for the purpose of stopping all loss by projections during the electrolysis. Thanks to these precautions there is not the slightest loss of metal.

We pour a mixture of 25 c.c. of nitric acid and 25 c.c. of water over the nickel, and cover the beaker immediately with a glass funnel, of which the edges rest on the interior of the beaker, and thus form a little gutter in which a few drops of water make a perfect hydraulic joint. Heat gently during the whole of the attack, and at the end raise the temperature to boiling. When the attack is finished withdraw the flame and leave the funnel in the glass for at least a quarter of an hour longer, so that the condensing vapours will wash or rinse the underside of the funnel. Then add 10 c.c. of H_2SO_4 and evaporate over a small flame until white sulphuric fumes are given off abundantly. There still remains a large excess of H_2SO_4 . Let cool and take up with water, then add ammonia in excess by 2 or 3 c.c. Boil for an instant to precipitate the iron completely, after having replaced the funnel in the beaker so as to stop projections. Then add 25 c.c. of ammonia at 22° , then a few c.c. of pure peroxide of hydrogen, which prevents the deposition of carbon with the nickel; dilute to 300 c.c., then electrolyse hot (at about 90°) with a current of 1 ampère with spiral and cylindrical electrodes; the cathode is made of platinum gauze dulled in the sand blast. After a few hours the nickel is all deposited. The rapidity with which the deposit is made is on account of the shape of our electrodes, and also because the metallic gauze allows a free circulation of the gases and the liquid.

The precipitate of silica and of the hydrates of iron and alumina present in the liquid does not interfere with the deposition of the nickel; on the contrary, the current frees this precipitate from the entangled nickel much more completely than would be done by filtration and repeated washings. Once the nickel is deposited, the precipitate is filtered and re-dissolved in the smallest possible quantity of sulphuric acid, neutralise with ammonia, which must be added in excess, and add the whole to the original solution. Electrolyse as before, using the same cathode already covered with almost the whole of the nickel. A test with sulphhydrate of ammonium will indicate the end of the electrolysis. While still leaving the electrodes hanging from their support, the beaker containing the electrolytic bath is withdrawn and replaced with a beaker filled with distilled water; the current must continue to pass for about five minutes, and this frees the gauze from all salts it might retain. The cathode is then plunged for a few minutes into a second beaker of distilled water, then into absolute alcohol; dry and weigh. In this manner we get the whole of the nickel and cobalt present in the original metal, as well as the copper. So the weight of the copper and the cobalt must be subtracted after being estimated, as will be described further on. As for the arsenic and the antimony, they remain with the hydrate of iron in the form of insoluble arseniate and antimoniate of iron.

Estimation of the Copper.—The electrolytic deposit just obtained is dissolved in a mixture of 50 c.c. of nitric acid at 36° and 50 c.c. of water. Electrolyse with a current of 1 ampère, after having diluted to 300 c.c. Weigh the deposited copper after having washed and dried it as described above.

Estimation of the Cobalt.—The nitric solution freed from copper is evaporated to a syrupy consistence on a sand bath. Take up with water, and make alkaline with potash, then dissolve in acetic acid; finally add 150 to 200 c.c. of a 50 per cent solution of nitrite of potash. After standing

all night the precipitation is complete; filter, wash with a solution of acetate and nitrite of potassium, then dissolve in a mixture of 1 volume of H_2SO_4 and 1 volume of water, and 3 to 4 volumes of hydrochloric acid. Evaporate until the appearance of abundant fumes of sulphuric acid. The sulphate of cobalt is then electrolysed under the same conditions as the nickel, already described.

Estimation of the Iron.—In the mother-liquors, freed from nickel, cobalt, and copper, there is still the precipitate of silica, alumina, and iron, as well as the arsenic and antimony. This precipitate is filtered, washed, and dissolved in dilute sulphuric acid. The antimony and the arsenic are precipitated by sulphuretted hydrogen, filtered and washed, then the sulphuretted hydrogen is driven off from the filtrate by heating. The liquid is treated with 5 grms. of citric acid, from 25 to 50 c.c. of a saturated solution of sulphurous acid, and 25 c.c. of ammonia at 22° ; then dilute sulphuric acid is added drop by drop until the solution is neutral. Make alkaline with a few cubic centimetres of ammonia, dilute up to 300 c.c., and electrolyse at a temperature of about 40° with a current of 1 ampère. After a short time the iron is deposited integrally. As it carries with it a little carbon and also a little platinum from the dissolution of the anode under the influence of the sulphurous acid, it cannot be weighed; it is therefore estimated volumetrically; for this purpose it is dissolved in dilute sulphuric acid, boiled and filtered (the filter retains the platinum and the carbon deposited with the iron, which would otherwise act on the $KMnO_4$), and left to cool in a current of CO_2 and in the presence of a small piece of zinc, sufficient to reduce the iron. When the whole of the zinc is dissolved and the solution is cold, it is titrated with permanganate of potash.

Estimation of the Alumina.—The mother-liquors from the electrolysis of the iron are evaporated to dryness with an excess of sulphuric acid. To destroy the remainder of the organic matter the residue is taken up with a mixture of equal volumes of sulphuric and nitric acids, then again evaporated to dryness. The residue is dissolved in water acidulated with hydrochloric acid, and the filtered solution is treated with hydrochlorate of ammonia and ammonia, then boiled. The alumina is precipitated, it is washed, filtered, and weighed in the state of Al_2O_3 .

Estimation of the Lime.—The mother-liquors which have been freed successively from the nickel, cobalt, iron, and aluminium, still contain the whole of the lime. These liquors are concentrated, but not sufficiently to cause crystallisation of the salts—then precipitated with oxalate of ammonia. The well-washed oxalate of lime is placed, with its filter, in a conical flask, and sulphuric acid at one-fifth strength (by volume) is added. The oxalic acid is titrated with permanganate of potash at 35° to 40° , after having added a little manganous sulphate to the flask to accelerate the action of the permanganate.

Estimation of the Magnesia.—The mother-liquors, free from lime, are treated with arseniate of soda, which precipitates the magnesia in the form of ammonio-magnesian arseniate. Filter, wash, and dissolve the precipitate in 150 c.c. of hydrochloric acid at 22° ; this solution is then distilled for arsenic in the presence of 15 grms. of ferrous sulphate (see Hollard and Bertiaux, *Bull. Soc. Chim.*, 1900, vol. xxiii., p. 300).

From the arsenic, estimated volumetrically, we calculate the magnesia, $MgO = As \times 0.538$.

Estimation of the Sulphur and the Silica.—Five to 10 grms. of the metal are attacked with nitric acid diluted with its own volume of water. Evaporate on the water-bath after having added about 25 c.c. of hydrochloric acid, and drive off the HNO_3 by repeated evaporations with hydrochloric acid. The residue is treated with 2 to 3 c.c. of hydrochloric acid, then with water. Filter to remove the silica and wash with warm water.

The filtrate contains only a portion of the sulphur, the other part being retained by the silica. The filter containing the silica is dried, then burnt with its contents, after impregnating them with a solution of nitrate of ammonia,

which prevents the formation of volatile sulphurous acid. The whole is fused with 2 grms. of carbonate of soda. After complete fusion, allow to cool, and treat the melted mass with water and hydrochloric acid in excess, evaporate to dryness on the water-bath, take up with 2 or 3 c.c. of hydrochloric acid, then with water, filter the silica and wash it with water. The filtrate which contains the sulphur present in the silica is added to the first filtrate, and the mixture is precipitated with chloride of barium at boiling temperature; allow to stand for a night in a warm place. Filter and weigh the sulphate of baryta.

As for the silica, it is dried, calcined, and weighed. It is then treated with hydrofluoric acid and a few drops of sulphuric acid. Evaporate, calcine, and weigh. From the loss of weight we calculate the amount of silica.

Estimation of the Carbon.—Proceed as for the estimation of the carbon in cast-iron or steel.

Estimation of the Arsenic.—Distil the arsenic by heating the nickel with ferric sulphate and hydrochloric acid. (see HOLLARD and BERTIAUX, *Bull. Soc. Chim.*, 1900, vol. xxiii., p. 300).

Estimation of the Antimony.—The liquid freed from arsenic by distillation, and which contains all the antimony, is treated with chloride of zinc, then distilled in a current of hydrochloric acid gas (see HOLLARD, *Ann de Chim. Analytique*, 1900, p. 330). The chloride of antimony distilled over is precipitated with sulphuretted hydrogen, and then estimated electrolytically (see *Bull. Soc. Chim.*, 1903, vol. xxix., p. 262).—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 22.

NOTICES OF BOOKS

La Grande Industrie Chimique Minérale. ("The Industries of Mineral Chemistry"). By E. SOREL. Paris: C. Naud. 1904.

THE subjects of which this volume treats include potassium, sodium, and the halogen elements and their compounds. The first chapters describe the properties and methods of extraction of sea salt and rock salt, and the preparation of potashes, iodine, and bromine. The preparation of sulphate of sodium is then considered, and the manufacture of hydrochloric acid. Considerable space is devoted to the description of the Leblanc soda process, which appears ill-advised when it is remembered that it is rapidly giving way to more recent and economical methods, though it may be some time before it is entirely superseded. The last part of the book deals with the manufacture of chlorine and the various recovery processes connected therewith. The information seems to be well up to date, and no doubt this volume will be found as useful as the preceding one by the same author, dealing with sulphur, nitrogen, and phosphorus, which appeared some two years ago.

Alfred Werner's Theorie des Kohlenstoffatoms und die Stereochemie der Karbocyclischen Verbindungen. ("Alfred Werner's Theory of the Carbon Atom, and the Stereo-chemistry of the Carbocyclic Compounds"). By Dr. ERNST BLOCK. Wien und Leipzig: Carl Fromme. 1903.

THIS short sketch of Werner's theory relating to the stereo-chemistry of the carbon compounds contains a very readable review and critical examination of the various theories of the structure of the benzene nucleus which have been put forward since the time of Kekulé. Regarding Werner's theory as the most satisfactory from every point of view, the author discusses it in detail, and upon the three formulae suggested by Werner, Vaubel, and Sachs respectively, finds a new benzene formula which appears to combine the advantages of all three. In some cases, Dr. Block shows a tendency to write as if the last word had been written on the subject, but the original sugges-

tions contained in the book are certainly worth noting. The constitutions of naphthalene, anthracene, phenanthrene, and pyrene are also shortly discussed in the light of the new benzene theory.

Hypochlorite und Elektrische Bleiche. ("Hypochlorites and Electrical Bleaching"). By VIKTOR ENGELHARDT. Halle-a-S.: Wilhelm Knapp. 1903.

THE author of this monograph has divided his subject into two parts, to be treated in separate volumes. Keeping in mind the very different requirements of the technical electro-chemist and the manufacturer, he has reserved for the second part all details regarding practical applications and the methods of examination chemically of the raw materials, while this volume is devoted to the consideration of the technical and constructive aspect of the subject. A great number of specifications of patents granted in most European countries, and in America, are abstracted, and details of apparatus described at some length with copious illustrations; a chronologically arranged tabular statement of the main features of the most important patents brings the subject down to 1902. The specifications have been grouped under different headings in such a manner as to simplify greatly the study of the subject, and the book is a model of conciseness and convenience.

Proceedings of the Chemical and Metallurgical Society of South Africa. With Appendix. February, 1897—September, 1899. Vol. II. Johannesburg: Published by the Society. Edinburgh: R. W. Hunter. New York: The Engineering and Mining Journal. Pp. 928.

THE belated appearance of this volume, which was published only in October last, is explained by the Secretary to be due to the late war. The volume, he says, would have been published earlier but for the fact that the "copy" was left in Johannesburg during the war, and that a large number of the members being on active service in the various irregular regiments during that period, it was impossible for some of the papers to be revised until their return.

The volume begins with a list of officers and council for 1897-98-99-1902, and a list of members and associates in September, 1899. Then follow the records of the monthly meetings from February 20th, 1897, to September 16th, 1899, the papers read at these meetings, and the discussions thereon. These meetings are of very great value to the mining industry, for it is here that the different managers and chemists interchange ideas and give each other, and the world at large, the benefit of their experiences.

We feel safe in asserting that never has a goldfield been conducted on such scientific lines as the Witwatersrand. The old rule-of-thumb methods have had their day, and a good one it was; but now that science has come to the assistance of blind experience, gold is being won from tailings, slimes, and even tail-waters, to an extent that would fairly astonish the old-time mining captains and prospectors.

These results have been brought about to a very large extent by the "Chemical and Metallurgical Society of South Africa," and we heartily congratulate the society on having got through the trouble and stress of a prolonged period of fighting, though with somewhat impaired ranks, and feel confident that their labours will be as progressive in the future as they were valuable in the past.

The Latin Grammar of Pharmacy. By JOSEPH INCE, F.C.S., F.L.S., F.G.S. Tenth thousand, Eighth Edition. London: Baillière, Tindall, and Cox. 1903. Pp. 371.

WE can imagine this volume being of use to medical and pharmaceutical students who have gone through their early school days without learning very much Latin, but to the average student who has had the usual liberal education, a

large part of this volume would be entirely superfluous. On the other hand, we doubt if a student of eighteen or nineteen years of age, who had not already learned Latin, would be able to do much good at so belated a period.

The first portion of the volume is simply an ordinary Latin grammar, but beginning with page 93 we come to the technical portion, "Essay on the reading of Latin prescriptions," followed by another on "Medical directions."

One of the most useful portions of the book is that containing the "reference vocabularies." This is in two parts, "Latin-English" and "English-Latin," and covers about 90 pages.

The book is conveniently arranged, and as a reference book it will no doubt be serviceable and worth a place on the book-shelf.

A Short Manual of Analytical Chemistry (Qualitative and Quantitative—Inorganic and Organic). By JOHN MUTE, Ph.D., F.R.S.E., F.I.C., &c. Ninth Edition, Illustrated. London: Baillière, Tindall, and Cox. 1903. Pp. 235.

THIS book, originally written for pharmaceutical students, has been so extended and improved as to rank as one of the most useful reference books extant for the general analytical practitioner. It is essentially not a book for beginners, and Chapter I. might be easily omitted as unnecessary. No extension has been made in this edition, but some alterations and improvements have been introduced as the result of experience. Advantage has also been taken of the use of certain new reagents (such as sodium peroxide) in simplifying manipulations.

CORRESPONDENCE.

WHAT MAY RESULT FROM THE STUDY OF RADIUM.

To the Editor of the Chemical News.

SIR,—Apropos of the interest evinced both by scientists and the public generally, as evidenced by their muster to listen to Sir Oliver Lodge recently, may I have the privilege of space to draw attention to an analogical position which existed about a century ago, when in 1815-1816, Dr. Prout propounded his famous and astounding theory, causing not less sensation than the historical prophecy of Sir William Crookes last summer at Berlin, who in concluding expressed the opinion that the atomic dissociation may again reduce matter to the protyle, the formless mist; and when speaking on the miracle of radium, as Mr. Boys, President of the Physical Section of the British Association, termed it in his address last September, called attention to the analogy between the electrons from radium and those emitted by comets, popularly called its "tail."

Dr. Prout's celebrated theory put in a nutshell was that the atoms of the various elements were the essence in more or less concentration of one primordial substance, which he took for argument as hydrogen. Thus, according to atomic weight, an oxygen atom would consist of 16 hydrogen atoms compounded, whilst 32 atoms of hydrogen would be required to produce one of sulphur. By supposing all these atoms to be of one uniform size, as inferred from Avogadro's law—"that equal volumes of gases contain the same number of molecules"—we had simply in the various elements physical compounds made up of atoms of uniform size, but of greatly varying potential. It was subsequently argued, particularly by Stas, who made some careful researches, that Prout's theory was unsound, or else the atomic weights of the various elements would be exact whole numbers, whereas there were fractions to be accounted for. Again, Dumas, in 1878, reverted to the "primordial atomic" theory, and brought arguments by which several of Stas's results were brought more

closely into line with Prout's theory. Others of no small repute as chemists and physicists have argued for and against the theory, which although, as far as I know, never satisfactorily refuted, has been allowed to lie dormant.

Now if it is established beyond argument, as Sir Oliver tells us, that atoms are composed of electrons, of which a thousand million million packed closely would be required to make an atom in bulk, and moreover from the experiments of Prof. Rutherford last February, it might be inferred that the Alpha rays of radium became another element (helium also of recent discovery), because the atomic weight of the electrons of those rays was twice that of hydrogen; which inference has now been set beyond doubt by Sir W. Ramsay and Prof. Soddy, having watched the spectrum of helium gradually develop in an excited vacuum tube into which only radium emanation had been placed. Further remarkable evidence of this change of state results from the observations by Sir Wm. and Lady Huggins, of the spectrum of radium in air, giving the spectrum line by line of nitrogen. And, as Prof. E. Rutherford says, the energy displayed by radium emanation must be internally stored up. Is not all this evidence marvellously analogous to the crude theory of Prout? And do not the researches of Prof. Rutherford and other leading scientists point to the time when, if not already present, the celebrated theory of our philosopher of nigh a century ago is on the very doorsteps of truth, and all atoms are made up of a simple substance, but of varying potential, even as the potential of radium is above that of any known substance, and is naturally falling, very, very, almost inestimably, slowly through the other states, each state of which constitutes another element?—I am, &c.,

H. BARKER LAKE.

77, Colmore Row, Birmingham.
January 14, 1904

WHY ARE SOME ELEMENTS SO MUCH MORE ABUNDANT THAN OTHERS?

To the Editor of the Chemical News.

SIR,—It is well known that different elements occur in very different quantities. Some elements are excessively rare, others are excessively abundant. Now what is the reason of this? Why are not all elements equally abundant? Is not perhaps a reason that some elements are more stable than others?

So that the most stable elements occur in the greatest quantity, the most unstable in minute quantities because, of the more rapid transformation of the unstable elements into other forms of matter?

A perusal of the researches of Sir William Crookes, Sir William Ramsay, and others certainly inspire such thoughts.

Indeed, the phenomena may be part of that universal decay of elements so grandly pictured by Sir William Crookes—the elements decaying at different rates, just as different substances evaporate at different rates. The bearing of such a conception upon geology and the past history of the earth is obvious. A slow continuous process acting for many ages can produce the mightiest effects.—I am, &c.,

GEOFFREY MARTIN.

Institute of Chemistry of Great Britain and Ireland.—Final (A.I.C.) Examination, April, 1904.—A Final Examination, in all branches except that of Biological Chemistry, will be held at the Laboratories of the Institute, commencing on Tuesday, the 12th day of April, 1904, provided that a sufficient number of Candidates enter their names for the same. The Examination will be open only to Candidates who have complied with the Regulations. Applications should be forwarded not later than Tuesday, the 23rd day of February, 1904. For further particulars apply to the Registrar, Institute of Chemistry, 30, Bloomsbury Square, London, W.C.

MEETINGS FOR THE WEEK.

- MONDAY, 25th.—Society of Arts, 8. "Cantor Lectures," "Oils and Fat—their Uses and Applications," by J. Lewkowitsch, Ph.D., &c.
TUESDAY, 26th.—Royal Institution, 5. "Development of Animals," by Prof. L. C. Miall, F.R.S.
WEDNESDAY, 27th.—Society of Arts, 8. "Ice-breakers and their Services," by Arthur Gulston.
THURSDAY, 28th.—Royal Institution, 5. "The Flora of the Ocean," by G. R. M. Murray, F.R.S.
FRIDAY, 29th.—Royal Institution, 9. "The Marshes of the Nile Delta," by David George Hogarth, M.A.
SATURDAY, 30th.—Royal Institution, 3. "The British Folk Song" (with Vocal Illustrations), by J. A. Fuller Maitland, M.A.

INSTITUTE OF CHEMISTRY
OF GREAT BRITAIN AND IRELAND.

Founded 1877. Incorporated by Royal Charter 1885.

FINAL (A.I.C.) EXAMINATION, APRIL, 1904.

A Final Examination in all branches, except that of Biological Chemistry, will be held at the Laboratories of the Institute, commencing on TUESDAY, the 12th day of APRIL, 1904, provided that a sufficient number of Candidates enter their names for the same. The Examination will be open only to Candidates who have complied with the Regulations. Applications should be forwarded not later than TUESDAY, the 23rd day of FEBRUARY, 1904.—For further particulars apply to the REGISTRAR, Institute of Chemistry, 30, Bloomsbury Square, London, W.C.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
JEWRY STREET, ALDGATE, E.C.

Principal—CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.

EVENING CLASSES IN CHEMISTRY, METALLURGY, PHYSICS, AND MATHEMATICS.

Designed to meet the requirements of those engaged in CHEMICAL, METALLURGICAL, and ELECTRICAL INDUSTRIES, and in trades associated therewith.

Every facility for Special and Advanced Practical Work in well-equipped Laboratories.

CHEMISTRY	{ CHARLES A. KOHN, M.Sc., Ph.D., F.I.C., and G. SENTER, B.Sc., Ph.D.
PHYSICS	R. S. WILLOWS, D.Sc., B.A.
METALLURGY	C. O. BANNISTER, Assoc.R.S.M.
MATHEMATICS	G. W. O. KAYE, B.Sc.

CLASSES IN METALLURGY.

GENERAL METALLURGY.

THE METALLURGY OF GOLD AND SILVER.

METALLOGRAPHY, including PYROMETRIC WORK.

ASSAYING.

ANALYTICAL CHEMISTRY,

Including ELECTROLYTIC and GAS ANALYSIS.

Each Course of Lectures will be accompanied by suitable Laboratory Work.

GLASS BLOWING.

Two Courses of Instruction will be given during the Lent Term by Mr. A. C. COSSOR.

New TERM begins MONDAY, JANUARY 4th,
1904.

The Institute is readily accessible, and near to Fenchurch Street, Liverpool Street, Broad Street, and Metropolitan Railway Stations.

For details of the Classes apply at the Office of the Institute, or by letter to the PRINCIPAL.

W. H. DAVISON, M.A.,

Clerk to the Governing Body.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC, As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, &c.

BIRKBECK COLLEGE

(BIRKBECK INSTITUTION),

Breems Buildings, Chancery Lane, E.C.

DAY AND EVENING SCIENCE CLASSES.—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board, Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.

INSTRUCTION IN

PURE CULTIVATION OF YEAST.
According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts brewers', distillers', wine, disease yeasts, moulds, and bacteria. *Manuals*: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jørgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufacturers, &c.

Further particulars on application to the Director—

ALFRED JØRGENSEN, The Laboratory, Copenhagen, V.

MICA

Telephone
No. 2248
Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., & London.
102 & 103, Minorities, E.C.,
MICA MERCHANTS.

Manufacturers of Mica Goods for Electrical and ALL purposes.
Contractors to His Majesty's Government.

THE CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free (including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

Five lines in column (about 10 words to line)	£ s. d.
Each additional line	0 3 6
Whole column	1 5 0
Whole page	3 0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

ABSOLUTE ALCOHOL,

FREE FROM DUTY,

FOR SCIENTIFIC AND RESEARCH WORK IN LABORATORIES

To be obtained from

HUGO LORENZ,

7-8, Idol Lane, Great Tower St., London, E.C.,

Licensed Trailer in Alcohol and Spirits of Wine.

Stock kept in suitable packages ready for immediate use.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2305.

THE CAUSES OF THE ANALOGY BETWEEN FLUORINE AND OXYGEN.

By GEOFFREY MARTIN, B.Sc. (Lond.)

MR. LENHER, in the *CHEMICAL NEWS* for December 24th, 1903, vol. lxxxviii., p. 307, showed that, whereas gold gives at ordinary temperatures a fairly stable chloride, the corresponding fluoride is very unstable, and he expressed some surprise that this should be so. The law underlying this observation is given below. Moissan some years ago (*Bull. Soc. Chim.*, 1891, [3], v., 880) pointed out that, of all the halogens, fluorine is the one which resembles oxygen most closely in its general properties and in its compounds.

Being curious to know what it is that causes fluorine to resemble oxygen more closely than chlorine or bromine does, I proposed to myself the following questions:—

A. Does not fluorine resemble oxygen more closely than chlorine resembles oxygen, because the fluorine approaches the oxygen more closely than the chlorine does, as regards the intensity of the force with which it attracts a given radicle? In other words, does not the chemical similarity of two elements arise from the fact that they both attract the same radicles with nearly the same intensity of force?

B. Seeing that chemically similar elements and compounds, as a rule, have about the same degree of volatility and fusibility, is not this because there is a connection between the intensity of the chemical forces which an atom is capable of exerting and the degree of volatility of the compounds into which it enters? And in particular, would not this connection exhibit itself among the fluorides, chlorides, and oxides, in such a manner that those compounds which approach each other nearest in the intensity of the force with which the atoms in the molecules are attracted together, be those which approach each other nearest as regards fusibility and volatility?

That is to say, is it not the internal atomic forces in the molecule which determine the external forces with which the molecules themselves are attracted together?

The answer to both questions is in the affirmative, as will be seen from the following data:—

A. First we will show that fluorine and oxygen approach each other more closely in the intensity of the force with which they attract the same radicles than do chlorine and oxygen.

This may be established by three lines of argument:—

- That founded on a comparison of the heats of formation of corresponding fluorides, chlorides, and oxides.
- That founded on the fact that O and F both tend to make an element with which they combine exhibit a higher grade of valence than Cl can make it exhibit.
- That founded on the chemical stability of corresponding fluorides, chlorides, bromides.

We will consider each briefly.

a. The heats of formation of the fluorides (so far as they are known) stand closer to the heats of formation of the corresponding oxides than to those of the corresponding chlorides. Thus, arguing that the intensity of force which holds the atoms together in the fluorides stands nearer to that which holds the atoms together in the corresponding oxides than in the corresponding chlorides.

For example, we have:—

(H, Cl) = 22; (H, F) = 37.6; (H, O₂) = 34.2.

b. Oxygen and fluorine both resemble each other in that

they tend to make the elements with which they combine exhibit a higher grade of valence than Cl can make them exhibit.

For example, the stablest oxide of Mn at ordinary temperatures is Mn₂O₃. Also, the stable fluoride is MnF₃, whereas the stablest chloride is MnCl₂, MnCl₃ being an excessively unstable body spontaneously decomposing at ordinary temperatures to MnCl₂ and Cl. Again, SO₃ is at ordinary temperatures a quite stable body, not parting with O below a red heat. Also SF₆ is a very stable body. Whereas SCl₆ is too unstable to exist at ordinary temperatures, and SCl₄ is only capable of existing below -26° C. Similarly, P₂O₅ is at ordinary temperatures by far the stablest oxide of P; so also PF₃ is the stablest fluoride of P; on the other hand, PCl₅ is easily decomposed to PCl₃.

The stablest oxide of I is I₂O₅, and the stablest fluoride is IF₅. But ICl₃ is so unstable that it seems incapable of existing at ordinary temperatures. ICl₃ is also unstable, easily decomposing when heated. Only ICl seems to be stable enough to bear heating. (Notice that the fluorides follow the oxides and not the chlorides as regards stability).

These facts can be best interpreted to mean that both O and F exert nearly the same intensity of force on an element, so that when O is capable of making the element give rise to a stable compound of a high valency grade, F is also capable of doing the same thing.

Whereas the intensity of the force exerted by Cl on the same element is much less, so that the corresponding high valency compounds of Cl are much less stable than those of O and F.

c. The chemical stability of compounds depends upon the intensity of the forces with which the atoms are attracted together in the molecule. We will show that when we contrast an oxide and the corresponding fluoride, on the one hand, with the same oxide and the corresponding chloride on the other, the oxide and fluoride approach each other much more closely as regards their stability than do the oxide and chloride. In fact, when the oxides of an element are unstable and the chlorides stable, then the fluorides follow oxides in being unstable. And conversely, when the oxides are stable and the chlorides are unstable, the fluorides follow the oxides in being stable.

So that O and F approach each other more closely than do O and Cl in the intensity of the force with which they attract the same radicles. We will now illustrate this.

1. The following examples show that when the oxides are less stable than the chlorides, the fluorides are also less stable than the chlorides:—

Na₂O, NaCl, NaF.—The fact that the heat evolved when Na combines with an equivalent of O is much less than the heat evolved when Na combines with an equivalent of Cl, (Na₂O₂) = 49.8, (NaCl) = 97.7, shows that Cl is attracted to the Na with a greater force than is O. The fact that NaCl is hardly acted on at all by superheated steam, whereas NaF is partially decomposed, indicates that in NaF the F is attracted to the Na with a force less than that with which the Cl is in NaCl.

K₂O, KCl, KF.—We have (K₂O₂) = 47.45, (KCl) = 104.7, so that KCl is very much more stable than K₂O. Also KCl is very much more stable than KF; for water at ordinary temperatures is capable of decomposing KF, whereas KCl is only decomposed by water at a red heat.

Ag₂O, AgCl, AgF.—We have (Ag, Cl) = 29.00, (Ag, O₂) = 2.950, which indicates that AgCl is very much more stable than Ag₂O. Again, Ag₂O is completely decomposed at 290°, whereas AgCl is not decomposed at 1735° (white heat).

Similarly, AgF is like Ag₂O, much less stable than AgCl, being completely decomposed to Ag when heated in the air.

It would appear from Mr. Lenher's results (*vide supra*) that AuF₃ in this respect resembles AgF, but is even more unstable than this body, because Au₂O₃ is more unstable than Ag₂O. See also below, HgF₂.

TABLE I.—Showing that Non-metallic Fluorides are more Volatile than Non-metallic Chlorides.

Compound.	Physical state.	Volatility.
PF ₃	Gas	—
PCl ₃	Liquid	Boils at 78°
PF ₅	Gas	—
PCl ₅	Solid	Sublimes at about 147°
POF ₃	Gas	—
POCl ₃	Liquid	Boils at 107.5°
SiF ₄	Gas	Boils at -107°
SiCl ₄	Liquid	Boils at 59°
BF ₃	Gas	—
BCl ₃	Liquid	18.5°
CF ₄	Gas	—
CCl ₄	Liquid	78°
SF ₆	Gas	Boils a little above -55°
SCl ₂	Liquid	Boils at +139°
SOF ₂	Gas	" -32°
SOCl ₂	Liquid	" +78.8°
SO ₂ F ₂	Gas	" -52°
SO ₂ Cl ₂	Liquid	" +82°
AsF ₃	Liquid	" 63°
AsCl ₃	Liquid	" 130°

TABLE II.—Showing that Non-metallic Oxides are usually more Volatile than the corresponding Chlorides.

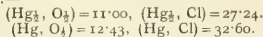
(Data is largely taken from HENRY, *Phil. Mag.*, 1885, [5], xx., 81).

Compound.	Physical state.	Volatility.
OO	Perfect gas, formerly considered permanent	B.p. -183° C.
OCl ₂	Gas, easily liquefied	" -17°
SO ₂	Gas	" -10°
SOCl ₂	Liquid	" +82°
SO ₃	Solid	" 46°
SO ₂ Cl ₂	Liquid	" 82°
CO ₂	Gas	Boils -78°
COCl ₂	Liquid	" 8°
CCl ₄	Liquid	" 76°
C ₂ Cl ₄ O	Liquid	" 118°
C ₂ Cl ₆	Solid	" 182°
POCl ₃	Liquid	" 110°
PCl ₅	Solid	" 148°
CO ₂	Gas	" -78°
CCl ₄	Liquid	" +76°

CuO , CuCl_2 , CuF_2 .—We have $(\text{Cu}_3, \text{Cl}) = 25.8$, $\text{Cu}_3, \text{O}_3 = 18.6$. So that Cl is more strongly attracted by Cu than is O.

So also the fluorides of Cu are very much more unstable than the chlorides, $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, for example, spontaneously decomposing in three or four days.

HgO , HgCl_2 , HgF_2 .—The oxides of Hg are less stable than the chlorides. For example, HgCl_2 can be vaporised without decomposition, whereas HgO easily decomposes when heated. The same appears from their heats of formation:



Also the fluorides of Hg are much less stable than the chlorides, both towards the action of water and of heat.

Thus the hydrated fluoride is decomposed at only 30°, and HgF_2 is decomposed at ordinary temperatures by H_2O .

HgF is decomposed to Hg and F when heated above 200°.

2. The following examples show that when the oxides are more stable than the chlorides, the fluorides are also more stable than the chlorides.

TABLE III.—Showing that the Metallic Fluorides are usually less Fusible than the corresponding Chlorides.

Compound.	Physical state.	Fusibility.
LiF	Solid	Melting-point.
LiCl	"	803°
NaF	"	598°
NaCl	"	902°
KF	"	772°
KCl	"	789°
RbF	"	738°
RbCl	"	753°
CuF	"	719°
CuCl	"	908°
AgF	"	434°
AgCl	"	435°
CaF ₂	"	457°
CaCl ₂	"	902°
SnF ₂	"	719°
SnCl ₂	"	902°
BaF ₂	"	825°
BaCl ₂	"	908°
MgF ₂	"	860°
MgCl ₂	"	908°
ZnF ₂	"	708°
ZnCl ₂	"	734°
CdF ₂	"	262°
CdCl ₂	"	520°
SbF ₃	"	541°
SbCl ₃	"	296°
ZrF ₄	"	73.2°
ZrCl ₄	"	White heat
		400°

SO_3 , SCl_6 , SF_6 .— SO_3 is a quite stable substance at ordinary temperatures, and only decomposes at a red heat. SCl_6 is at ordinary temperatures too unstable to exist, even SCl_4 only exists below -20°. SF_6 is like SO_3 quite stable even at a red heat.

B_2O_3 , BCl_3 , BF_3 .—We have $(\text{B}_4, \text{O}_4) = 52.8$, $(\text{B}_4, \text{Cl}) = 34.6$, showing that B_2O_3 is very much more stable than BCl_3 . A comparison of the chemical behaviour of the two substances confirms this conclusion. BCl_3 , for example, is easily decomposed by heat and various chemical reagents, such as water; B_2O_3 , however, is stable at the highest temperatures, and is not decomposed by heating with carbon.

Similarly, BF_3 is very much more stable than BCl_3 . It is not (like BCl_3) decomposed by electric sparks, nor by Fe at a red heat.

Al_2O_3 , AlCl_3 , AlF_3 .— Al_2O_3 is very much more stable than AlCl_3 . Also AlF_3 is very much more stable than AlCl_3 being, unlike the latter, unacted upon by air, acids, or alkalis. AlF_3 resembles Al_2O_3 rather than AlCl_3 in appearance, properties, and stability.

Mn_2O_3 , MnCl_3 , MnF_3 .— Mn_2O_3 and MnF_3 are both, at ordinary temperatures, perfectly stable bodies. MnCl_3 , however, is excessively unstable, spontaneously decomposing at ordinary temperatures into MnCl_2 and Cl.

The first question we have proposed must therefore be answered in the affirmative, namely, fluorine resembles oxygen more closely than does chlorine, because the fluorine atom attracts a given radicle with an intensity of force which approaches nearer that which oxygen exerts on the same radicle than does that which chlorine exerts.

And therefore that the chemical similarity of two elements arises from the fact that both attract the same radicles with nearly the same intensity of force.

This latter conclusion I have confirmed in the case of almost every set of elements in the periodic table which

TABLE IV.—*Showing that Metallic Oxides are usually less Volatile and Fusible than the corresponding Chlorides.*
(Data largely taken from a compilation by HENRY, *loc. cit.*.)

Compound.	Physical state.	Fusibility.	Volatility.
NbCl ₅	Solid	Fuses at 194°	Boils at 240·5°.
Nb ₂ O ₅	"	Infusible	Fixed.
TaCl ₅	"	Fuses at 211·3°	Boils at 241·6°.
Ta ₂ O ₅	"	Infusible	Fixed.
Al ₂ Cl ₆	"	Very fusible	Boils at 180°.
Al ₂ O ₃	"	Fusible in OH flame	Fixed.
FeCl ₃	"	Fuses at 306°	Easily volatile.
Fe ₂ O ₃	"	Infusible	Fixed.
CrCl ₃	"	—	Volatile.
Cr ₂ O ₃	"	Infusible	Fixed.
CrO ₂ Cl ₂	Liquid	—	Boils at 118°.
CrO ₃	Solid	Fuses about 300°	Decomposes.
WCl ₅	"	Fuses at 248°	Boils at 275·6°.
WCl ₆	"	" 275°	" 346·7°.
WCl ₆ O	"	" 210·4°	" 127·5°.
WO ₃	"	" a red heat	Fixed.
VC ₄	Liquid	Does not solidify at -18°	Boils at 154°.
VO ₂	Solid	—	—
VOCl ₃	Liquid	Does not solidify at -15°	Boils at 126·7°.
TeCl ₄	Solid	Fuses at 224°	Boils at 414°.
TeO ₂	"	Fusible	Less volatile than tellurium.
AsCl ₃	Liquid	Does not solidify at -29°	Boils at 134°.
As ₂ O ₃	Solid	Volatile without fusion	" 200°.
SbCl ₃	"	Fuses at 73·2°	Boils at 225°.
Sb ₂ O ₃	"	" red heat	Volatile below 156°.
SbCl ₅	Liquid	Solid at 0°	Volatilises with SbCl ₃ and Cl ₂ .
Sb ₂ O ₅	Solid	Non-fusible	Non-volatile.
BiCl ₃	"	Fuses at 227°	Boils at 427—439°.
Bi ₂ O ₃	"	Fusible	Fixed.
HgCl ₂	"	Fuses at 265°	Boils at 295°.
HgO	"	Infusible	Decomposed at red heat.
Hg ₂ Cl ₂	"	Sublimes at 400—500° without melting	—
Hg ₂ O	"	Infusible	Decomposes.
Cu ₂ Cl ₂	"	Fuses at 434°	Boils at 954—1032°.
Cu ₂ O	"	" a red heat	Fixed.
CuCl ₂	"	Fuses at 498°	Decomposes.
CuO	"	Fuses at bright red heat with decomposition	"
PbCl ₂	"	Fuses at 498°	Boils at 861—954°.
PbO	"	Fuses about a red heat	Volatile at white heat.
AgCl	"	Fuses at 451°	—
Ag ₂ O	"	Infusible	Decomposes.
CaCl ₂	"	Fuses at 719°	—
CaO	"	Infusible	Fixed.
SnCl ₂	"	Fuses at 825°	—
SnO	"	Infusible	Fixed.
BaCl ₂	"	Fuses above 860°	—
BaO	"	Fusible in OH flame	Fixed.
MgCl ₂	"	Melts at 708°	Volatile.
MgO	"	Infusible	Fixed.
ZnCl ₂	"	Fuses at 262°	Boils at 676—683°.
ZnO	"	Infusible	Fixed.
CdCl ₂	"	Fuses at 541°	Boils at 861—954°.
CdO	"	Infusible	Fixed.
UCl ₄	"	—	Volatile.
UO ₂	"	Infusible	Fixed.

betray a striking resemblance to each other. But the results of this research will be set forth elsewhere.

B. We now proceed to deal with the second question.

The accompanying tables show that the corresponding fluorides and oxides approach each other more closely as regards volatility than do the corresponding chlorides and oxides:—

Table I. shows that non-metallic fluorides are more volatile than the non-metallic chlorides.

Table II. shows that the non-metallic oxides are more volatile than the non-metallic chlorides.

Table III. shows that metallic fluorides are usually less volatile than the corresponding metallic chlorides.

Table IV. shows that the metallic oxides are also less volatile than the corresponding metallic chlorides.

In other words, those compounds which approach each other nearest in the intensity of the force with which the atoms are attracted together in the molecule (viz., the oxides and fluorides) are precisely those which approach each other nearest as regards volatility and fusibility.

That is to say, it is the intensity of the internal atomic forces with which the atoms are attracted together in the molecule which determines the intensity of the external attractive force between molecule and molecule, and therefore the volatility of the compound.

This seems a very important conclusion.

A wider research embracing the compounds of all the elements has convinced me that this law is true in its generality. But the results of this research must also be set forth elsewhere.

University of Kiel, December 26, 1903.

USE OF BISMUTH AS A MEANS OF SEPARATION IN THE RARE EARTH SERIES.

By G. URBAIN and H. LACOMBE.

IN a preceding research (*Comptes Rendus*, vol. cxxxvii., p. 792) we established the fact that bismuth, when employed in the fractionation of double magnesium nitrates, acts as a separating element between samarium and gadolinium. M. Demarçay's europium exists only in minute quantities as compared with gadolinium and samarium in the rare earths, but we have now been able to assign a place to this element in the separation. In our first experiments, however, we started with too small a quantity of material.

Since then we have repeated the experiments with large quantities of oxide. We find that by examination of the absorption spectrum of europium and of its spark spectrum, bismuth inserts itself exactly between samarium and europium.

Bismuth therefore apparently divides the two large groups of the rare earths, and from this we see that europium can be considered as the first term of the series of the yttria earths.

We have therefore utilised, for a new type of separation, the property of the isomorphism of bismuth magnesium nitrate with the same salt of the rare earths. The principle of this method is deduced from the following facts:—

When a series of isomorphous salts give non-crystallisable mother-liquors, the proportion of salt capable of crystallisation retained in the mother-liquors depends on the mass of the non-crystallisable salt accompanying it. Reciprocally, when a large quantity of salt capable of crystallisation is in the presence of a small quantity of non-crystallisable salt in a state of purity, a measurable quantity of this latter is retained in the crystallisation, *à fortiori*, very soluble salts, but nevertheless susceptible of separate crystallisation. Thus the non-crystallisable mother-liquor of magnesium nitrate always retains a proportion of gadolinia, which can be as much as a third of the contained earths. Demarçay considered the fractionation of the

double sodium sulphates to eliminate yttria as one of the most satisfactory methods.

In our method we do not require the multiple treatments which the above method of fractionation necessitates.

If the same weight of magnesium nitrate of bismuth is added to the non-crystallisable mother-liquors, the added salt retains the gadolinium during its crystallisation. The operation should be repeated until the soluble earths give no spark spectrum of gadolinium.

This method of retention recalls the method proposed by Auer von Welsbach to extract from neodymium the last traces of praseodymium by the addition of pure lanthana. But if, in our separation, the bismuth plays an analogous rôle to that of the lanthanum in Auer von Welsbach's method, it is not so inconvenient, since the bismuth can with such great facility be separated from the rare earths in the subsequent operations.

This method of extraction of the gadolinium earths can equally well be used to eliminate gadolinium from crude yttria earths in which this element is present only in small proportion, as in the earth xenotime.

The methodical fractionation of the bismuthic gadoliniferous nitrates in the same order in which they have been obtained allows of the rigorous separation of the ceric and yttric earths. The insolubility of the magnesium nitrates of the earths which precede samarium in the solution of the double nitrate of bismuth allow of the separation of these earths from soluble samaria with an almost quantitative yield.—*Comptes Rendus*, vol. cxxxviii., p. 84.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, January 9th, 1904.

SIR,—Of the 203 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford during December shows a considerable falling off. The amount of rain actually measured is 0.97 inch; the average fall for the month is 2.16 inches. Thus we have a deficit of 1.19 inch, which, if deducted from the previous excess of 11.74 inches, leaves a total excess for the year of 10.55 inches, or 41.7 per cent on the thirty-five years' average.

TABLE I.—Rainfall in Inches at Oxford, Month by Month, during the Year 1903.

	Actual fall.	Mean of 35 years.	Difference from the mean	
	Inches.	Inches.	Inches.	Inches.
January ..	2.58	2.08	—	+0.50
February ..	0.79	1.00	—1.01	—
March ..	3.03	1.47	—	+1.56
April ..	2.28	1.61	—	+0.67
May ..	4.38	1.75	—	+2.63
June ..	5.58	2.10	—	+3.48
July ..	3.47	2.49	—	+0.98
August ..	3.34	2.38	—	+0.96
September ..	1.54	2.39	—0.85	—
October ..	6.41	2.76	—	+3.65
November ..	1.47	2.30	—0.83	—
December ..	0.97	2.16	—1.19	—
	35.84	25.29	—3.88	+14.43

Our bacteriological examinations of 366 samples taken during last month have given the results recorded in the

TABLE II.—Showing the Average Monthly Bacterial Variations during the Year 1903.

Month.	Thames, unfiltered.	Thames-derived Companies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered.	River Lea (East London), filtered.
January	13161	61	319	13	313	38
February	15653	23	455	8	254	10
March	9337	27	335	11	582	29
April	2820	15	141	6	193	20
May	4625	19	231	11	351	26
June	10337	42	151	7	474	28
	9122	32	273	9	361	25
July	3805	23	258	11	261	36
August	1090	43	270	15	189	33
September	6202	39	333	19	337	29
October	16671	66	843	30	470	25
November	18390	43	845	25	610	28
December	27216	37	861	40	226	18
	13866	41	563	23	347	28
	11594	36	420	16	354	26

Mean of 1st 6 months.

Mean of 2nd 6 months.

Mean of 12 months.

TABLE III.—Average Number of Microbes in the Filtered London Waters for the Past Seven Years.

	Thames-derived Companies.	New River.	River Lea.
1897	46	32	62
1898	34	30	25
1899	27	15	20
1900	21	9	10
1901	24	10	22
1902	27	13	25
1903	36	16	26

TABLE IV.—Averages of the Supplies derived from the River Thames during the Year 1903

	Common salt per gallon. Means.	Nitric acid per gallon. Means.	Hardness. Degrees. Means.	Oxygen required per gallon. Means.	Organic carbon per gallon. Means.	Organic carbon per gallon. Maxima.	Colour. Brown: Blue. Means.
January	2 335	1'149	16 56	0'064	0'191	0'293	25'5 : 20
February	2 391	1'040	17'07	0'056	0'165	0'255	20 5 : 20
March	2 360	0'911	15'96	0'063	0'190	0'281	21 9 : 20
April	2'204	0'779	14'77	0'050	0'154	0'250	14 6 : 20
May	2'083	0'701	14'29	0'066	0'192	0'299	19 5 : 20
June	1'919	0'605	14 13	0'062	0'189	0 338	23 4 : 20
July	1'956	0'700	15'61	0'066	0'155	0'251	20 6 : 20
August	2'029	0'626	15'16	0'054	0'148	0'194	14'6 : 20
September	2'166	0'707	15 63	0'055	0'164	0'246	14'2 : 20
October	2'019	0 731	15'08	0'083	0'229	0 400	26 8 : 20
November	1 937	0'719	16 78	0' 88	0 245	0 388	29 8 : 20
December	2'029	1'025	16'74	0' 66	0 205	0 244	22 3 : 20

following table. Besides these samples we have examined 362 others from special wells, standpipes, &c., making 728 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	861
New River, filtered (mean of 75 samples) ..	40
Thames, unfiltered (mean of 24 samples) ..	27,216
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 194 samples) ..	37
Ditto ditto highest ..	376
Ditto ditto lowest ..	0
River Lea, unfiltered (mean of 24 samples) ..	226
River Lea, from the East London Water Company's clear-water wells (mean of 24 samples) ..	18

Of the 293 daily samples taken from the general filter wells of the Metropolitan Water Companies, sixteen samples, or 5·4 per cent, were sterile. Thirty-one samples, or 10·5 per cent, contained more than 100 microbes, and of these, nine samples contained more than 150 microbes per c.c. The thirty-one excess samples contained an

average of 156 microbes per c.c. In November thirty samples contained an average of 168 microbes per c.c.

The above figures show that the bacterial condition of the unfiltered water was worse than in November, but that of the filtered supply was much better.

During the past year we have examined 8022 samples of London waters bacteriologically, as compared with 6953, 6893, and 6731 respectively in the three previous years. We have also made 2614 chemical analyses of London waters throughout this period, making a total of 10,636 samples examined during the year.

Table II. gives the bacteriological results for the past year. During the first six months the Thames-derived Companies' clear-water wells contained on an average 32 bacteria per c.c., while the New River and River Lea supplies contained respectively 9 and 25. During the second six months the numbers of bacteria in the waters from the same three sources were 41, 23, and 28 respectively.

Table IV. gives the average chemical composition of the Thames-derived supplies during the year 1903. The relatively exceptional high values of the organic carbon during the autumn months is to be attributed to the greatly excess-

sive rainfall, causing the solution of considerable amounts of vegetable matter, naturally associated with an increase of colour in the supply. Considering the abnormal meteorological conditions, the filtration of the London waters has been on the whole successfully carried out. So far as the Returns of the Registrar-General show, the conditions of Public Health have been highly satisfactory, and it is interesting to note that there has been no suggestion of the occurrence of any water-borne disease.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

REPORT ON ASH.*

By G. S. FRAPS.
(Concluded from p. 43).

Work of H. C. Sherman on Sulphur and Phosphorus.

H. C. SHERMAN, of Columbia University, New York City, during the past summer has been studying the methods for the determination of sulphur and phosphorus in organic materials. We have had some correspondence on the subject, and he has kindly communicated to me the results of his work, which will appear in the *Journal of the American Chemical Society*. The methods which Dr. Sherman has studied are as follows:—

1. Combustion in oxygen under pressure of 25 to 30 atmospheres in the bomb calorimeter.
2. Fusion with alkali, as described by Osborne.
3. The provisional method of this Association (the nitric acid method), with the use of 2 grms. of sample.

Six samples of material were used. In every case the nitric acid method gave lower results than the other two methods, the average amount of sulphur found being about five-sixths of that present. It seems probable that the greater part of the discrepancy is due to volatilisation of sulphur in some form of combination not sufficiently oxidised to stand the heat generated at this point. Such a loss could doubtless be avoided by repeated evaporation with nitric acid, or by the addition of alkali along with the nitrate, but the method would thus become practically that of Salkowski. Combustion in oxygen has the advantage over the fusion method.

The fusion method is described by Osborne as follows (*Journ. Am. Chem. Soc.*, 1902, xxiv., 142):—

About 10 grms. of sodium peroxide were converted into hydroxide in a nickel crucible by adding a little water and boiling over an alcohol lamp until the excess of water was expelled. From 1 to 2 grms. of the protein were then stirred into the slightly cooled hydroxide, and oxidised by gradually raising the heat and adding small portions of sodium peroxide until the oxidation was complete. The fused mass was then dissolved in 400 c.c. of water, its solution strongly acidified with hydrochloric acid, boiled until the excess of peroxide was destroyed and chlorine expelled, filtered, made neutral with ammonia, and an excess of 4 c.c. of concentrated hydrochloric acid added. From the boiling solution sulphuric acid was precipitated by gradually adding a solution containing 1 gm. of barium chloride. After standing overnight on a steam table the barium sulphate was filtered out, washed, ignited, and weighed.

Dr. Sherman uses 15 grms. of sodium peroxide, and with vegetable materials the acidulated solution was evaporated to dryness, and heated to dehydrate any silica which might have been present.

This method differs from that tested by the referee chiefly in the use of a larger volume of water in the solution from which the barium sulphate was precipitated.

As it is well known that barium sulphate is soluble in strong solutions of salts, it is possible that this may account for the difference.

Dr. Sherman exchanged samples with the referee, with the following results. The sample of lean meat was sent by Dr. Sherman. The other two samples are the referee's samples:—

TABLE V.—Comparison of Methods for the Determination of Sulphur.

Method and analyst.	Lean meat.	Cotton-seed meal.	Corn bran.
	Per cent S.	Per cent SO ₃ .	Per cent SO ₃ *
Compressed oxygen method—Sherman	0.82	1.49	0.47
Fusion method—Sherman . . .	0.81	—	—
Nitric acid method—Sherman . . .	0.68	—	—
Nitric acid method—Fraps	0.57 0.52	1.03 1.07	0.40 0.41

I am convinced by this work that the nitric acid method gives too low results.

Determination of Potash.

The results obtained by the different analysts for potash by the methods already described are as follows:—

TABLE VI.—Potash Determinations.

Analyst.	Corn bran.		Cotton-seed meal.	
	Method I. Sulphuric acid.	Method II. Charring and extracting.	Method I. Sulphuric acid.	Method II. Charring and extracting.
	Per cent.	Per cent.	Per cent.	Per cent.
J. H. Gibboney	0.43	0.39	1.80	1.82
	0.42	0.39	1.78	1.82
E. G. Runyan	0.37	0.38	1.61	1.73
	0.38	0.36	1.56	1.68
	—	—	1.60	1.72
R. W. Thatcher	0.42	0.37	1.64	1.77
	0.45	0.38	1.74	1.64
			—	1.72

There seems to be a slightly larger quantity of potash obtained by charring and extracting than by ignition with sulphuric acid, though the results are not conclusive.

Determination of Sulphates.

It has been suggested to the referee that not the total sulphur but the sulphur existing as sulphates in plants should be considered as the sulphur of the ash, since the organic sulphur would otherwise be counted twice. It is necessary, however, that we should have a method for the determination of total sulphur, in order to estimate the quantity of that element required by the growing plant; the fact should not be lost sight of for an instant that the determination of sulphur in an ash, as heretofore made, throws no light whatever upon the quantity of sulphur in the plant, and, since it leads to false conclusions, is worse than valueless.

That part of the sulphur in plants exists as sulphates, and part in the organic form, has been known for a long time. R. Arendt, in 1856, was the first to distinguish between organic and inorganic sulphur in plants, and to estimate total sulphur with any degree of accuracy. He extracted the sulphates with acidulated water, and estimated the total sulphur by fusion with alkalis. Ulricht pursued a similar plan. Arendt (1857) found small amounts (0.04–0.06 per cent) of sulphates in the lower leaves and ears of the oats, and more in the upper leaves (0.22–0.44 per cent). Ulricht (1859) states that sulphates are totally absent from the lower leaves and stems of red clover, while present in the upper leaves and the blossom.

Wolf and his associates (1859) give the following

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

quantity of sulphates and organic sulphur as present in the dry matter of green rape.

TABLE VII.—Distribution of Sulphur in Green Rape (Wolf).

Part of plant.	Organic sulphur. Per cent S.	Sulphates. Per cent SO ₃ .
Seeds	1.127	0.020
Straw	0.167	0.021
Chaff	0.310	1.464

Wolf and Yelin (1860) did not find any sulphates in the grain or straw of wheat, in barley, oats, or lucerne. Knop and Ritter (1859) found sulphates in garden beans (0.14 per cent), but none in the bean straw.

E. Schulze (*Landw. Versuchs. Stat.*, 1876, xix., 172) investigated the changes in sulphur during the sprouting of the seeds of the yellow lupine. The finely ground material was completely extracted with warm water, acidified with hydrochloric acid after separating a small quantity of albumen, and precipitated with barium chloride. As the precipitate did not appear pure it was fused with sodium carbonate with the addition of a little potassium nitrate, the melt extracted with water, and the sulphuric acid precipitated with barium chloride. The seed contained 1.028 per cent sulphur, 0.154 per cent as sulphates (0.385 per cent calculated as SO₃). The sprouted seeds contained 1.510 per cent and 1.703 per cent sulphur as sulphates after twelve and fifteen days respectively. An oxidation of organic sulphur took place during the germination.

Tammann (*Ber.*, 1886, xix., 261, Ref.) obtained 0.359 per cent SO₃ from peas, by fusion with sodium carbonate and saltpetre, and 0.075 per cent SO₃ precipitated by barium hydroxide from the hot water extract purified with tannic acid. After germinating twenty-five days, 0.191 per cent SO₃ was present—a decided increase. By boiling the alkaline filtrate from the barium sulphate with hydrochloric acid a second precipitate appeared, due, he says, to the presence of ethereal salts of sulphuric acid. The quantity of this second precipitate from the ungerminated seeds was insignificant as well as from the seeds germinated in darkness, while from those germinated in the light it corresponded to 0.019 per cent SO₃.

Berthelot and Andre (*Biedermann's Central-Blatt*, 1891, 555) investigated the sulphur in different forms in plants at different stages of growth. They concluded that the sulphur content of the plant increases continuously until it blossoms. The amount of sulphur present in organic compounds reaches its maximum at the time of flowering, and then gradually decreases partly on account of re-oxidation of the sulphur, partly by elimination of volatile sulphur compounds. The proportion of the two forms of sulphur in the seeds varies considerably in different species of plants. In *Avena sativa* nearly all the sulphur is present in the organic form; on the other hand, in the white lupine only 6.7 per cent of the total sulphur is in organic combination.

I have gone thus fully into the literature in order to give a clear idea as to the present standing of the determination of sulphates in plants. It is seen that the quantity of sulphates present may vary considerably, both in the seeds of different plants, different parts of different plants, different parts of the same plants, and in the same plant at different stages of growth. At times, indeed, the amount of sulphates present as sulphates is very small.

The following method was used for the determination of sulphates in several materials:—

Five grms. substance was mixed well with 50 c.c. of a 1 per cent solution of hydrochloric acid, allowed to stand half-an-hour, filtered, and washed with the dilute acid to 250 c.c. or more. The liquid was heated to boiling, barium chloride was added, and the determination completed in the usual way.

Instead of the 1 per cent hydrochloric acid, water was used in several cases, but it was found to dissolve organic

matter which was afterwards precipitated on coming in contact with the acid.

No sulphur as sulphates was found in the following materials:—Corn, peas, green millet, timothy hay, corn silage, peanuts.

Sulphur as sulphates was found in the following:—Oats (trace); crimson clover straw, 0.003 per cent; cotton-seed meal, 0.001 per cent; green cowpea vines, 0.085 per cent.

Determination of Chlorine.

The writer has already called attention to the fact that chlorine as well as sulphur will be lost in burning a plant substance to an ash by itself. It will appear later that the loss is due to decomposition of the chlorides by the heated organic matter.

Chlorine was determined in a number of substances in two ways, namely, in the ash as prepared in the usual way and by fusion of the plant material with sodium hydroxide, a method which will be described in full later on in this paper. The results of the determination are as follows:—

TABLE VIII.—Chlorine in Plants.

Material	Ash method. Per cent	Sodium hydroxide method	
		Per cent	
Corn	trace	0.040	
Peas	0.005	0.008	
Peas, No. 2	0.001	0.012	
Oats	0.005	0.007	
Oats, No. 2	0.001	0.056	
Peanuts	0.008	0.017	
Cotton-seed meal	0.008	0.032	
Cotton-seed hulls	0.005	0.013	
Linseed meal	0.010	0.029	
Millet	0.120	0.187	
Corn silage (dry)	0.310	0.607	
Green rape (dry)	1.261	1.290	
Green peas (dry)	1.160	1.205	
Sweet potatoes (dry)	1.341	1.362	
Timothy hay	1.864	1.888	

It is evident that a considerable proportion of the chlorine in plants may be lost in burning them to an ash, particularly when there is only a small quantity of chlorine in the plant.

The cause of the loss is shown by the work of Davies, reported in the *Journal of the Society of Chemical Industry*, (1901, xx., 98). He experienced similar losses when sugar, starch, or filter-paper was ignited with sodium chloride. The alkalinity of the ash was evidence that no base had been lost, and if the sodium chloride was added after the sugar had been charred, and the ignition then completed, no loss took place; that is to say, the loss took place during the initial stages of the combustion, and not during the time the carbon was being burned off, and was probably due to the decomposition of the chlorides by the hot vapours from the organic matters. Extracting the material with hot water after charring and then completing the combustion can therefore have no effect on the loss of chlorine, since it takes place before the extraction. When sodium carbonate equivalent to 5 per cent of the organic matter was added to the material, the loss of chlorine was prevented.

Three methods for the determination of chlorine in plants were tested:—

1. Ignition of the Material with Calcium Acetate.

Five grms. substance were moistened with 20 c.c. of a solution of calcium acetate containing 0.56 gm. calcium oxide, evaporated to dryness, and ignited. The ash was dissolved in nitric acid, filtered, and chlorine determined in the filtrate by the Volhard method. On account of the very small quantity of chlorine present in many of the substances, a gravimetric method could not be used, as the precipitate would not coagulate. The results by this method are low (Table IX.).

2. Fusion with Sodium Hydroxide.

Five grms. substance were mixed thoroughly with 20 c.c. of a solution of 100 grms. caustic soda in 200 c.c. water, evaporated to dryness, and finally fused. A nickel crucible was used for a portion of the work and silver crucibles for the remainder, due care being taken to prevent silver from being detached from the crucible. It is better to use nickel crucibles, as there is always a little danger of small particles of silver being detached. The melt was dissolved in water, neutralised with nitric acid, filtered, and chlorine determined in the filtrate by the Volhard method.

The method yields satisfactory results, but it is long, and the crucibles wear out rapidly.

3. Ignition with Sodium Carbonate.

Five grms. substance in a platinum dish are impregnated with 20 c.c. of a 5 per cent solution of sodium carbonate, evaporated to dryness, and ignited as thoroughly as possible. The residue is extracted with hot water, filtered, and washed. It is returned to the platinum dish, ignited to an ash, dissolved in nitric acid, and the chlorine determined by the Volhard method.

In one or two cases the filtrate from the first extraction was yellow from organic matter. It was returned to the dish with the charred residue, evaporated to dryness, and ignited. The residue burned very readily to a white ash. The sodium carbonate method gives as accurate results as the method of fusion with caustic soda, and as it is shorter and easier, it is to be recommended for use.

The results by the three methods are contained in the following table:—

TABLE IX. Methods for Chlorine.

Material	Ignition with calcium acetate Per cent	Fusion with caustic soda Per cent	Ignition with sodium carbonate Per cent
Corn	0.002	0.040	0.027
	—	0.040	0.026
Millet	0.148	0.165	0.188
	—	0.171	0.194
	—	0.204	—
Corn silage ..	0.400	0.616	0.610
	—	0.599	—
Cotton-seed meal	0.031	0.032	0.020
Cotton-seed hulls	0.010	0.013	0.017
Green peas ..	0.215	0.197	0.228
	—	0.212	0.239
Oats	0.034	0.056	—
Timothy hay ..	0.870	0.914	0.897
	—	0.878	0.911
	—	0.872	—

Recommendations.

The referee makes the following recommendations:—

1. Either that the method of fusion with sodium hydroxide and sodium peroxide be adopted as a provisional method by this Association, or else that the referee on ash be requested to make a further study of the fusion method.

2. That the method of determining chlorine by ignition with sodium carbonate be adopted as a provisional method.

A NEW METHOD FOR THE ATTACK OF
GALENAS AND CHALCOPYRITES.

BY C. BOUCHER.

When we have to estimate all the elements of a galena or a chalcopyrites, we often experience much difficulty in finding a sufficiently rapid and complete method for dissolving the mineral. We do not propose here to refer to all the well-known methods for the attack of these minerals, as most of them have come to be, in a way, classic. However, they are not always very convenient to carry out, most of these methods requiring a considerable time. We

think we have overcome this drawback in the method we are about to describe.

We have had recourse to the action of persulphates, salts which easily give up their oxygen, and of which the acid is fairly energetic. A first series of assays by the wet method, which consisted in boiling the sample of mineral with a concentrated solution of persulphate of ammonium, did not give very satisfactory results.

Still, after a certain time, the sulphide of lead of the galena is completely transformed into sulphate; a change which is also brought about, but less quickly, with sulphate of ammonium, as has been shown by Mascazzini.

By adding to the solution a few drops of concentrated nitric acid, the reaction becomes more rapid, and succeeds also with chalcopyrites. In all cases with this latter mineral the formation of spongy sulphur, which takes a long time to get rid off, becomes an annoying obstacle.

It is necessary then to boil for a long time on a sand-bath, to evaporate almost to dryness to melt the sulphur, and then to make certain that the resulting globule of sulphur does not contain any more of the mineral.

A second series of experiments made by the dry way gave excellent results. As reagent we used a mixture of 3 parts of persulphate of sodium* and 1 part of nitrate of ammonium, more or less approximately. The use of persulphate alone is insufficient, even in the cold galena gives off sulphuretted hydrogen on contact with these salts.

1. Treatment of Galenas.

We operate on 1 or 2 grms. of the well-powdered mineral, mixed more or less intimately, by means of a platinum wire, with four or five times its weight of the above-mentioned reagent; these amounts are only approximate. The operation may be performed either in an iron crucible, if the estimation of the iron is not indispensable, or in a sufficiently large porcelain crucible.

The mass must not occupy more than one-third of the crucible, which must be covered. The whole is then placed on a moderately heated sand-bath. After five or six minutes the crucible is removed, allowed to cool, and examined to see that the attack is complete (in this case no more black grains of galena will be visible). It suffices now to take up with water, and filter. On the filter we shall find the lead in the form of sulphate, mixed with the gangue, silica, &c., which are separated by the known methods. As for the sulphuric solution, it contains the other metals.

To better follow the progress of the reaction, and also to avoid all loss, we may very advantageously effect the fusion in an Erlenmeyer flask of Jena glass, about 100 c.c. capacity, for example, taking care to shake from time to time, and not to heat too strongly at the commencement.

II. Treatment of Chalcopyrites.

We operate on, say, 1 grm. of the powdered sample, passed through a fine sieve. Mix as above with 4 or 5 parts of the reagent. Place the whole, by preference, in a Kjeldahl matras of Jena glass. The neck of the matras presents projections, as the reaction is fairly lively. Heat on a sand-bath, or directly over a Bunsen flame. It is most essential to heat very moderately at the commencement, regulating the heat carefully. When the deflagration is over, we may heat more strongly, shaking the matras from time to time so that the fragments thrown up on the sides do not escape the reaction. The heat is continued until the reaction is finished (about five or six minutes); no more black grains should then be seen at the bottom of the matras.†

As soon as the reaction commences the mass takes a greenish-blue colour, due to the formation of sulphate of copper: this is a rapid means for distinguishing between a pyrites and a chalcopyrites. When the attack is

* Taken in preference to the ammonium salt, as it is more stable. This latter salt, in fact, decomposes fairly rapidly with heat.

† See our remark relative to Mn.

complete, allow to cool by spreading the mass over the sides of the matras. Take up with hot water, heat gently if necessary, and filter to separate the gangue (SiO_2). We obtain thus a sulphuric solution in which the metals can be estimated by the known methods.

It is unnecessary to add that this method requires a separate estimation of the sulphur.

Remarks.

If the minerals analysed contain any notable quantity of manganese, we must not forget that this metal will be found in the residue, in the form of MnO_2 .

We may recall the experiments made by Marshall, who showed that manganese is precipitated from its acid solutions (nitric or sulphuric) in the form of MnO_2 by boiling persulphates. (See also M. Dittrich and C. Hassel, *Berichte*, 1902, vol. xxxv., p. 3266, on this subject).

If a first tentative attack of the mineral does not succeed completely, we may very well add a further quantity of the reagent. In all cases it is not necessary to attach too much importance to the slight greenish-black residue left by some minerals (especially by chalcopyrites) after this attack, and of which the appearance may be similar to that of the mineral itself. It is generally composed of the unattackable gangue mixed with sulphur. However, for greater security, it is advisable, after taking up the fused and cooled mass with water, to filter rapidly without pouring out the residue, and after washing to treat the latter with a few drops of concentrated nitric acid. This solution, with the wash waters, is added to the principal solution, throwing the final residue on to the filter.

It may be asked, have the persulphates any action on glass? This has not been taken into consideration in view of the short time the reaction lasts. If necessary, platinum vessels could be used instead of glass ones. The truth will be inquired into later on.

As for the other sulphurised minerals, at least the pyrites, blendes, stibines, mispickel, &c., they have not furnished satisfactory results. They appear to be much more stable with the persulphates than are the galenas and chalcopyrites.

A curious thing about these latter is that they are much less easily attacked by acids than the former. Pyrites, especially, almost entirely resists the reagent used above.

Blendes are attacked very incompletely, and the reaction is accompanied by little explosions and the burning of the sulphur.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 18.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, January 22nd, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

MR. W. BENNETT read a paper entitled "Notes on Non-homocentric Pencils, and the Shadows produced by them. I. An Elementary Treatment of the Standard Astigmaticencil."

It is shown that several of the properties of the standard astigmatic pencil, and the variations in the form of its cross section, can be simply deduced from a consideration of the projections of its rays upon two planes, each of which is at right angles to one of the two focal lines. The projection of the rays are in each case concurrent. The shadow of a straight wire at right angles to the axis is also dealt with, and it is shown that the rays intercepted by the wire are one set of generators of a hyperbolic paraboloid. The section of this surface by any other plane is a hyperbola or a parabola. The rays are seen to be all parallel to a plane through the axis. If the object wire is not at right angles to the axis the shadow surface is a hyperboloid of

one sheet. The section by any plane is, in general, a hyperbola, which is rectangular when the plane is at right angles to the axis, and reduces to two straight lines when the plane passes through either of the focal lines. The asymptotes of the rectangular hyperbolas lie in two planes which pass respectively through the two focal lines. The author showed string models of the various pencils and shadow surfaces, and of pencils produced by lenses or mirrors. The paper concludes with a simple method for obtaining, by the method of sagittæ, the positions of the approximate lines produced in a small pencil refracted obliquely through a lens.

Prof. S. P. THOMPSON congratulated the author, and said that although many people accustomed to these pencils could easily follow the passage of the rays by the inspection of diagrams, there could be no doubt that there were others to whom the subject could only be made clear by the use of models. Geometrical models had an advantage because they could be so constructed as to show the characteristics of the particular aberration under consideration, a condition of things which could not be realised in the case of actual pencils produced by the passage of light through a lens system. The study of the peculiar shadows produced by these beams was one of the out of the way branches of physics which could be pursued with advantage. The results were so striking that they often engendered a curiosity leading to a further study of optics.

Prof. J. D. EVERETT expressed his interest in the paper and in the way the author had investigated the shadow phenomena by obtaining the equation to the ruled surface generated by the shadow of the rod. He drew attention to another point in the paper. Although a sloping rod generally gives a curved shadow, it is always possible to rotate the screen and get a straight shadow.

Mr. R. J. SOWTER said that in constructing a string model of the standard elliptic-sectioned beam, it was convenient to thread the strings between two lines representing the focal lines, and to obtain the corresponding points in the focal lines by projection from circles, since the points moved along the focal lines according to a simple harmonic motion rule. Further, it was useful to take stereoscopic photographs of the string models, so that the solid effects could be reproduced in the stereoscope, and the models thus replaced by the photographs.

The AUTHOR, in reply to Prof. Thompson, said the geometrical method gave results very simply when the aberration was purely astigmatic, but was less readily applicable when other aberrations were present. The formation of shadows could then be more readily followed by considering the form of the wave front, the way in which it meets the object wire, and the consequent evolutions of the trace left upon it by the object wire. Replying to Mr. Sowter, he said that the general method of constructing the models was simplified in many cases, both end plates being produced from a single easily-constructed template.

A paper by Prof. R. W. WOOD on "Some New Cases of Interference and Diffraction" was ready by the SECRETARY.

In this paper Prof. Wood discusses certain types of the interference of light which have been known for many years, as well as some cases which he thinks are quite new. The colours of mixed plates, and the phenomena of interference in transparent films deposited on metallic reflectors are the cases chiefly considered. The facts which have been brought out may be summed up as follows:—The colours of mixed plates are due to diffraction, and should not be classed with interferences in their films. The explanation originally given by Young, and the treatment given by Verdet and others, are unsatisfactory, and do not indicate what becomes of the energy. In the cases of films deposited on perfectly reflecting surfaces, which, according to the elementary theory, should exhibit no interference colours, we may, under certain conditions, have colours far more brilliant and quite as saturated as any shown by the soap bubble. In other cases, where at first sight no interference appears to have

taken place, we may, by employing polarised monochromatic light, obtain fringes of a very curious nature, which are the result of the interference between the elliptical vibration coming from the metal surface and the plane-polarised vibration reflected from the surface of the transparent film. The Secretary showed by means of the lantern the colours produced by reflection from thin films of mica and collodion deposited on silver. He also showed the polarised fringes produced by the interference of two streams of light polarised at right angles. The incident sodium light polarised at an angle of 45° with the plane of incidence was reflected from a wedge-shaped film of gelatin deposited on speculum metal, and the fringes viewed with an analysing Nicol.

Mr. JULIUS RHEINBERG said that Prof. Wood's paper had been of special interest to him; in particular as he found in it confirmation of the results afforded by some experiments he had made some time ago. He thought it was not generally known that some striking examples of the colours of mixed plates were to be found in Nature. A few years ago there had been some discussion in the Quekett Microscopical Club as to the origin of certain brilliant colours shown by the diatom *Actinocyclus Ralfsii* when seen with an objective of small numerical aperture. From an optical point of view, the diatom valves in question might be looked upon as plates of colourless siliceous material perforated by numerous tiny holes, and he had explained the matter as being a natural case of the colours of mixed plates. Mr. Rheinberg exhibited a number of specimens of *Actinocyclus Ralfsii* under the microscope.

A paper by Mr. S. SKINNER "On the Photographic Action of Radium Rays" was taken as read.

It is well known that a photographic plate by exposure to radium rays is affected in such a way that the plate develops similarly to its development after exposure to light. The experiments described in the paper are an attempt to answer the question: Are the actions the same? As far as can be seen, the final results of the actions and developments are the same, and the experiments appear to indicate that only slight differences occur in the early stages. The plates, suitably enclosed, were subjected to the rays from varying quantities of radium bromide for varying times, and the results showed that the intensity of the developed image increased rapidly to a maximum value with increase of exposure, then decreased, first rapidly, and finally very slowly until a stage was reached in which there was practically no dark image formed on development. It is found that spark images are at first obliterated by radium rays which do not cause such a great density as that of the spark images obliterated, and that with prolonged exposure the radium rays reverse the spark images.

Mr. W. A. PRICE exhibited a number of instruments constructed by Messrs. Crompton and Company.

The instruments shown were chiefly switches, galvanometers, and potentiometers, and Mr. Price explained that the chief interest of the exhibit lay in the mechanical devices which had been introduced to overcome difficulties of design.

Royal Institution.—On Thursday next, February 4, Mr. A. D. Hall, at 5 o'clock, delivers the first of three lectures at the Royal Institution on "Recent Research in Agriculture"; and on Saturday, February 6, at 3 o'clock, Mr. Charles Waldstein commences a course of two lectures on (1) "The Study of Style in Greek Sculpture," (2) "Culture and Sculpture"; and on Saturday, February 20, Lord Rayleigh begins his course of six lectures on the "Life and Work of Stokes." The Friday Evening Discourse on February 5 will be delivered by Mr. Alfred Austin, the Poet Laureate, his subject being "The Growing Distaste for the Higher Kinds of Poetry; the discourse on February 12 will be delivered by Dean Robinson on "Westminster Abbey in the Early Part of the Seventeenth Century"; and on February 19 by Mr. C. T. R. Wilson on "Condensation Nuclei."

CORRESPONDENCE.

WHY ARE SOME ELEMENTS SO MUCH MORE ABUNDANT THAN OTHERS?

To the Editor of the Chemical News.

SIR,—With regard to the suggestion of your correspondent, Mr. Geoffrey Martin, that the varying abundance of the elements may be due to the decay of the less stable, is not our actual knowledge of the material of the universe at present too limited to admit of any satisfactory attempt to answer this question? Is not our real knowledge of matter limited to a mere egg-shell crust of this planet, and the outer envelopes of the sun and stars? If the earth were once in a fluid state, it seems reasonable to suppose that the heavier elements would seek the centre of the mass. May it not well be that the core of the planet consists of gold and platinum, osmium and iridium, while further from the centre there may exist a layer of uranium and radium, tungsten, and so on, the small quantities of these elements found at the surface having been thrown up in the tremendous internal commotions which must have been constantly occurring, similar to the disturbances in the sun which produce sun-spots at present? The principal elements detected in the sun's surface are amongst those of least specific gravity and greatest volatility, and the inference is that the heavier elements are more deeply seated in the body of the sun.

Or, again, when the nebula from which our system was formed was contracting and breaking up into sun and planets, is there any reason why that small fraction which became our earth should necessarily have been a fair sample of the whole nebula? Or, indeed, need we suppose that the elements were originally formed in equal proportions?—I am, &c.,

J. C. KINGDON.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxvii., No. 25, December 21, 1903.

PRIZE NUMBER.

The Jecker Prize is awarded to L. BOUVEAULT for his researches in organic chemistry. His chief researches during later years were on the condensation of aldehydes with ordinary acetone leading to the synthesis of unsaturated ketones. He has also investigated the complex question of camphor and the terpenes and prepared a new liquid hydrocarbon, besides investigating the constitution of compounds of the isolaric and β -camphenolic series.

The La Caze Prize is given to M. GUNTZ for his various researches on general chemistry. His later researches have been connected with the electrolytic preparation of lithium, by which method he has prepared large quantities of the metal, and so been enabled to investigate its properties more fully.

No. 26, December 28, 1903.

Density of Chlorine.—H. MOISSAN and BINET du Jassoneix.—The authors find that if the density of chlorine is taken by Dumas' method, when the chlorine is prepared under ordinary conditions, the density varies between 2.424 and 2.506. The principal causes of error in these determinations are (1) the presence of air in the density bulb and in the current of chlorine, led through the

ions is -0.454 volt, that of the cupric ions -0.329 , ($H=0$). The equilibrium between the cupric ions and iodine can be expressed by the formula $2Cu^{++} + 2I^- = 2Cu^+ + I_2$.

	Product of solubility.	Energy of formation.	Heat of formation.
CuCl	$1.20-10^{-6}$	30'000	32'900
CuBr	$4.15-10^{-8}$	22'300	25'000
CuI	$5.06-10^{-12}$	16'600	16'300

—Zeit. Anorg. Ch., vol. xxxi., p. 458.

Simultaneous Volumetric Estimation of Boric Acid and Strong Acids.—W. Herz.—The principle of this method consists in titrating the strong acid by using an indicator on which the boric acid is without action. An estimation of the boric acid is then effected, after the addition of alcohol, mannite, or glycerin, by titrating in the usual manner with phenolphthalein. The indicator used for the titration of the strong acid is nitrophenol; the colourless solution becomes yellow in the presence of an excess of alkali. The following figures show what results may be expected by this method:—

Composition of the mixture—

HCl ..	13'0	6'5	19'5	6'5	26'0	21'7
B ₂ O ₃ ..	7'78	3'89	1'945	5'83	1'945	1'945
Found—						
HCl ..	13'0	6'5	19'4	6'45	26'0	21'75
B ₂ O ₃ ..	7'78	3'99	1'99	5'73	1'99	1'945

—Zeit. Anorg. Ch., vol. xxxiii., p. 353.

Chemical Study of the Culture of Chrysanthemums.—A. Hébert and G. Truffaut.—The authors find that three elements are necessary: nitrogen, phosphoric acid, and potash. Chrysanthemums are particularly greedy for phosphoric acid; this substance acts particularly on the formation of chlorophyll. Potash also plays an important part; it provokes turgescence of all the organs. Finally, nitrogen is an indispensable element; its absence causes the formation of rachitic and chlorotic plants. An excess of nitrogen is frequently the cause of cryptogamic maladies. —Bull. Soc. Chim., Series 3, xxix., No. 12.

MEETINGS FOR THE WEEK.

MONDAY, Feb 1st.—Society of Arts, 8. (Cantor Lectures). "Oil and Fats—their Uses and Applications," by J. Lewkowitch, Ph.D., &c.

— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 2nd.—Royal Institution, 5. "Development of Animals," by Prof. L. C. Miall, F.R.S.

— Faraday Society, 8. "Notes on Aluminium Welding," by Sherard Cowper-Coles. "Some Applications of the Theory of Electrolysis to the Separation of Metals from one another," by A. H. Holland.

WEDNESDAY, 3rd.—Society of Arts, 8. "Steam Cars for Public Service," by Thomas Clarkson.
— Society of Public Analysts, 8. (Annual Meeting). President's Address. "Note on the Quantitative Estimation of Mechanical Wood Pulp in Paper," by C. E. Cross and E. J. Bevan. "Note on Chinese Tall-oil Seed Oil," by L. Middleton Nash. "Note on the Analysis of Jam," by Raymond Ross.

THURSDAY, 4th.—Royal Institution, 5. "Recent Research in Agriculture," by A. D. Hall, M.A.
— Chemical, 8. "The Tautomeric Character of the Acidic Thiocyanates," by R. E. Doran. "The Resolution of α -Dihydroxybutyric Acid into its Optically Active Constituents," by R. S. Morrell and E. K. Hanson.

FRIDAY, 5th.—Royal Institution, 9. "The Growing Distaste for the Higher Kinds of Poetry," by Alfred Austin, B.A.

SATURDAY, 6th.—Royal Institution, 3. "The Study of Style in Greek Sculpture," by Charles Waldstein, Litt.D.

Gentleman with small capital, fully qualified
Chemist, with good Analytical and Technical experience, desires Partnership in Analytical and Consulting or small Manufacturing business in or near London.—Address, G. B. CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

HERNE BAY GAS & COKE COMPANY, Ltd.

TAR.

The Directors of the above Company are prepared to receive Tenders for the Surplus TAR produced at their Works at Herne Bay, Kent, from Jan. 1st to Dec. 31st, 1904.

It is estimated that the quantity will be about 35,000 gallons. Particulars of Contract and Form of Tender to be obtained from the SECRETARY, at 6 Bream's Buildings, Chancery Lane, London, E.C.

Tenders, quoting prices free on rail and in barge, in purchaser's own casks, to be sent in on or before SATURDAY, the 6th FEBRUARY proximo.

The Directors do not bind themselves to accept the lowest or any Tender.

H. E. NEWTON, Secretary.

January 25th, 1904.

HERNE BAY GAS & COKE COMPANY, Ltd.

SULPHURIC ACID.

The Directors of this Company are prepared to receive Tenders, on or before SATURDAY, the 6th FEBRUARY proximo, for the Supply of about 40 Tons of SULPHURIC ACID, to be delivered during the year 1,04.

Particulars of Contract and Form of Tender to be obtained from the SECRETARY, 6, Bream's Buildings, Chancery Lane, London, E.C.

The Directors do not bind themselves to accept the lowest or any Tender.

H. E. NEWTON, Secretary.

January 25th, 1904.

THE CHEMICAL NEWS

AND JOURNAL OF PHYSICAL SCIENCE.

Edited by Sir WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free, including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

Five lines in column (about 20 words to line)	£	s.	d.
Each additional line	..	..	0 3 6
Whole column	..	..	1 15 0
Whole page	..	..	3 0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1s. 6d. each.

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

MICA

Telephone
No. 2248
Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E. & London.
102 & 103, Minories, E.C.

MICA MERCHANTS.
Manufacturers of Mica Goods for Electrical and ALL purposes.
Contractors to His Majesty's Government

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC.
As described in the "Report of the Inland Revenue Departmental Committee on Arsenic Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, &c.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2306.

THE ESTIMATION OF UNBURNT PRODUCTS IN CHIMNEY GASES BY MEANS OF A MODIFIED ORSAT APPARATUS.

By WILLIAM H. SODEAU, B.Sc., F.I.C.,
Elswick Works and Walker Shipyard, Newcastle-on-Tyne.

In experimental work on the economic application of fuel, it is very desirable to know, whilst a trial is actually proceeding, not only what excess of air is being employed, but also the amount of unburnt gases.* Combining these data with the indications of a thermo-junction placed at the base of the funnel, one can follow throughout the trial the total amount of heat (potential as well as actual) which is passing up the chimney. With a given boiler, for example, if one takes care of the exit gases, the evaporation will practically take care of itself. The fuel employed represents a certain total amount of heat, and the loss by radiation from the boiler will be practically uniform; hence the evaporation per pound of fuel may be gauged by what remains after deducting the various losses from the calorific value of the fuel, or, in other words, by working up the chimney gas results as in a "heat balance sheet."

This method of checking the evaporative efficiency is especially advantageous in short experimental runs, as feed water is not always read with much accuracy, and all that passes through the main stop valve may not actually be steam.

The actual analytical problem may be reduced to the rapid determination of carbon dioxide, carbon monoxide, and hydrogen (including hydrocarbons if present). It is, however, customary to determine the oxygen in chimney gases, whilst the estimation of hydrogen is usually omitted. The desirability of determining the amount of hydrogen is illustrated by the table below, in which are given a few analyses of the products of incomplete combustion obtained in some experiments with a 1000 horse-power water-tube boiler of the "Express" type. With Welsh coal the loss as unburnt hydrogen usually amounted to nearly a third of the loss as carbon monoxide, whilst with petroleum the proportion averaged about two-thirds. This difference was no doubt mainly due to the larger proportion of total hydrogen present when oil-fuel was employed.

Air being practically constant in composition it is unnecessary to estimate the oxygen in chimney gases if the approximate composition of the fuel is known, for it is then easy to work out simple formulæ by means of which those data which are of practical importance may be calculated with fair accuracy from the percentages of carbon dioxide, carbon monoxide, and hydrogen alone.

* When working with very limited furnace space, as in naval water-tube boilers of the "Express" type, a reduction of the "excess" of air may cause large amounts of combustible gases to escape unburnt, and so lead to decreased, instead of increased, evaporative efficiency.

Take, for example, two analyses of fuels:

	Welsh coal.	Texas petroleum.
Carbon	88.2	85.0
Sulphur	0.77	1.34
Hydrogen	2.6	12.0
Ash, oxygen, &c.	8.43	1.66

Theoretical amount of air for 1 pound fuel	100.0	100.0
	11.1 lbs.	13.95 lbs.

Using CO₂, CO, and H₂ to respectively denote the percentages of carbon dioxide, carbon monoxide, and hydrogen in the chimney gases, the following formulæ may be obtained by calculation from the equations for combustion:—

1. Pounds air per pound of fuel—

$$\frac{20.1}{\text{CO}_2 + \text{CO}} + 0.28 = \frac{20.6}{\text{CO}_2 + \text{CO}} + 0.84$$
2. Excess air per cent above theoretical—

$$\frac{18.37 - 9}{\text{CO}_2 + \text{CO}} - 97.5 = \frac{14.76 - 7.4}{\text{CO}_2 + \text{CO}} - 94.1$$
3. Evaporation units lost as unburnt gases—

$$\frac{9.33}{\text{CO}_2 + \text{CO}} + \frac{\text{CO} + \text{H}_2}{\text{CO}_2 + \text{CO}} = \frac{9.04}{\text{CO}_2 + \text{CO}} + \frac{\text{CO} + \text{H}_2}{\text{CO}_2 + \text{CO}}$$

These formulæ will, of course, apply only to fuels having the composition given above. For ordinary purposes the terms including CO may be omitted from the numerators of formulæ (1) and (2). Curves can then be plotted having CO₂+CO on one axis, and either "pounds air per lb. of fuel" or "excess air per cent above theoretical" on the other, so that the meaning of an analysis can be seen at a glance.

An ordinary Orsat apparatus affords a ready means of estimating the carbon dioxide, but the absorption of carbon monoxide by means of that somewhat objectionable reagent, cuprous chloride, involves the previous removal of oxygen by means of phosphorus or alkaline pyrogallol, absorbents which act exceedingly slowly when too cold. This method takes no account of free hydrogen (or saturated hydrocarbons). The author decided to discard absorption by cuprous chloride in favour of a combustion method, and not finding the capillary combustion tube of palladised asbestos (as fitted in the Orsat-Lunge apparatus) quite suitable for use in the stokehold, finally adopted an Orsat apparatus modified as shown in the accompanying figure, in which the main feature is an adaptation of the Winkler combustion pipette.*

A large glass stopcock, s, of 4 to 5 m.m. clear bore, is attached to the base of the apparatus, one end being connected to the measuring tube and the other to the reservoir, M. R. The pipette, K, is of the ordinary form, and contains caustic potash solution (one part potash to two of water). A similar pipette, P, containing phosphorus or alkaline

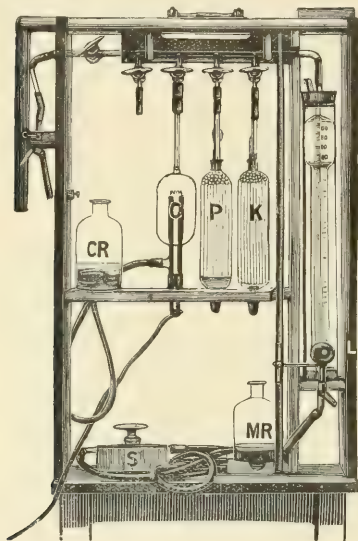
* The Winkler pipette, a development of Coquillon's "Grisometer," is described and figured in Winkler and Lunge's "Technical Gas Analysis," pp. 251-253.

Examples of Incomplete Combustion.

	Welsh coal.				Crude Texas oil (steam sprayed).			
Carbon dioxide, per cent	9.0	11.0	9.9	9.2	6.1	9.5	9.0	7.0
Carbon monoxide, per cent	2.15	2.8	1.65	1.3	2.1	1.5	1.0	0.6
Hydrogen, per cent	0.65	0.55	0.47	0.4	1.2	1.0	0.6	0.4
Pounds air per pound fuel	17.2	14.7	17.75	19.5	25.7	19.45	21.35	25.0
Excess air per cent above theoretical	55.0	32.3	60.0	75.7	84	39	53	79
Evaporation units* per pound of fuel lost as combustible gases	2.34	2.26	1.71	1.51	3.65	2.05	1.45	1.06

* An "evaporation unit" is the amount of heat required to convert one pound of water at 100° C. into steam at the same temperature.

pyrogallol, may be used if it is desired to estimate the oxygen. The combustion pipette, *c*, may be made from the commercial form of Winkler pipette by simply cutting off the U-tube and sealing on a straight piece of capillary tube of suitable length. An ordinary Hempel pipette for solid absorbents may be altered in a similar manner, the neck at the bottom being closed by a two-holed indiarubber stopper through which passes a pair of unlaqueured brass electrodes bridged across by a platinum spiral made by coiling about 4 c.m. of platinum wire of about 0.3 m.m. diameter around a needle 1.3 m.m. thick.



When the combustion pipette is employed with mixtures rich in combustible gases the coil must be near the top of the bulb in order that serious explosions may be avoided, but for the analysis of any ordinary chimney gases the coil may be placed much lower in order to reduce the heating of the glass. The gas may then be returned as soon as the current is cut off, without waiting for the glass to cool.

A fixed bulb* as in the Hempel (or Orsat) pipette, may be employed to receive the displaced water unless it is desired to carry out the rapid estimation of carbon monoxide and hydrogen together, as described below, when the bulb, *c*, should be connected by means of indiarubber tubing to the reservoir, *CR*, consisting of a small aspirator bottle, similar to that connected to the measuring tube. When in use the spiral is raised to a white heat by means of a two-cell accumulator, the current being conveniently adjusted to the right strength by passing it through a few feet of the tinned iron wire, about $\frac{1}{16}$ inch diameter, which is commonly sold in penny skeins.

In order to eliminate parallax the measuring tube is read by means of a lens mounted in conjunction with an eyecap, and sliding on a brass rod, as employed in connection with the "Kew principle" correction tube (*Journal Soc. Chem. Ind.*, 1903, xxii., pp. 188, 189). Before each reading

is taken, the water in the measuring tube is allowed to drain down for one minute, as indicated by the sand-glass used for timing the absorptions and combustions.

The U-tube filled with glass wool ordinarily supplied with the Orsat apparatus being somewhat apt to clog if dense black smoke is produced, it is conveniently replaced by a simple T piece having a small plug of glass wool in the limb through which the sample enters the apparatus. In this way only the actual samples are filtered, and the solid particles in the main stream pass direct to the aspirator.

Method of Analysis.—The measuring off of the sample is effected in the usual manner, except that it is convenient to close *s* instead of pinching the indiarubber tube when adjusting the water to the zero mark prior to bringing the gas to atmospheric pressure.

Carbon dioxide is estimated by sending the greater part of the gas over into *k* and back again, then leaving it for one minute to complete the absorption, and measuring again as usual; the decrease gives the percentage of carbon dioxide. The current is next switched on, and the gas passed over into the combustion pipette, *c*, where it remains for one minute, being then returned to the measuring tube (after switching off the current), and the contraction noted.

The carbon dioxide produced is then determined by a one minute absorption in the potash pipette, *k*; the decrease gives the percentage of carbon monoxide.

As carbon monoxide unites with half its volume of oxygen to form its own volume of carbon dioxide, it follows that half the amount of the carbon monoxide found must be deducted from the contraction during combustion. Two-thirds of the corrected contraction equals the percentage of hydrogen.

For example, if the contraction on combustion amounted to 2.3 c.c. and the resulting carbon dioxide to 1.6 c.c., then the gas contained 1.6 per cent of carbon monoxide and $\frac{2}{3}(2.3 - \frac{1.6}{2}) = \frac{2}{3} \times 1.5 = 1.0$ per cent of hydrogen. It

should be noted that the only absorbent employed is one which is readily obtained and seldom needs renewing. The estimation of carbon dioxide, carbon monoxide, and hydrogen by the above method can be completed in fifteen minutes. Any traces of hydrocarbons, if present, will of course appear partly as carbon monoxide and partly as hydrogen in the above method of analysis. Their heat value will not be fully represented, but this is an unimportant defect, and it exists more markedly in the old cuprous chloride method.

It may occasionally be desirable to know the percentage of oxygen originally present in the gas. This may be found by finally absorbing with phosphorus or pyro in the pipette, *p*, and adding to the result the amount of oxygen required to burn the combustible gases.

Rapid Joint Estimation of Carbon Monoxide and Hydrogen.—This may be carried out by omitting the measurement immediately after combustion, and transferring the gas direct from *c* to *k* in the following manner:—After the carbon dioxide has been determined, open the stopcock attached to *c*, and switch on the current, raising the reservoir, *MR*, so as to drive the gas into *c*. Close *s* when the water has risen to the top of the measuring tube, and about one minute later switch off the current and open the stopcock of *k*, raising the reservoir, *CR*, so as to drive the gas over into the potash, and finally closing the stopcock of *c*. After allowing one minute for absorption, the stopcock, *s*, is opened, the residue drawn back into the measuring tube, and the stopcock of *k* then closed. Two-thirds of the contraction so produced equals the percentage of "combustible gases," *i.e.*, carbon monoxide and hydrogen, in the sample.

The result so obtained is translated into "evaporation units" by means of a formula similar to 3, the denominator being replaced by $\text{CO}_2 + (\frac{2}{3} \times \text{combustible gases})$ in the case of Welsh coal, and by $\text{CO}_2 + (\frac{1}{3} \times \text{combustible gases})$ when

* The ordinary Hempel pipette is sometimes supplied with a bulb too small to contain the water displaced by the heated gas.

Texas oil is employed. The amount of air is similarly found by means of formulæ or curves.

When collecting samples of chimney gas for subsequent analysis the sometimes troublesome process of saturating water during the trial may be avoided by appropriately diluting a saturated solution of carbon dioxide. Thus, if the gas is expected to contain about 12 per cent of carbon dioxide, the sample bottles should be filled with a mixture of seven parts tap-water and one part of water saturated with carbon dioxide. The flow of water from the sample bottle may be conveniently regulated by attaching, say, a yard of tubing (in order to give a fairly uniform head), to the end of which is connected a "wash-bottle jet" which has previously been found to permit the emptying to take place in the required time. The jet is less likely to clog if used in the reversed position.

PRECIPITATION AND SEPARATION BY WEAK ORGANIC BASES.*

By E. T. ALLEN.

(Continued from p. 44).

Separation of small quantities of Alumina from excess of Iron.

THE first precipitation in the following series was made in a nearly neutral solution of about 150 c.c. volume. After washing out most of the iron by the phenylhydrazine sulphite solution, the precipitate was dissolved on the filter in a few cubic centimetres of hot dilute hydrochloric acid, washed through with hot water, neutralised with ammonia, and acidulated with 2 or 3 drops 1:1 HCl. The precipitate which is thrown down in a small volume of liquid by 0.5 c.c. phenylhydrazine, is washed with the sulphite solution till free from iron. After blasting, the precipitate is usually pure white.

No.	FeCl ₃ taken.	Fe ₂ O ₃ .	AlCl ₃ taken.	Al ₂ O ₃ .	Al ₂ O ₃ found.	Error.
	Cc.	Grm.	Cc.	Grm.	Grm.	Grm.
1.	35	= 0.2189	0.1	= 0.0005	0.0005	+0.0000
2.	35	= 0.2189	0.2	= 0.0010	0.0014	+0.0004
3.	35	= 0.2189	0.6	= 0.0030	0.0031	+0.0001
1'.	35	= 0.2189	0.7	= 0.0007	0.0008	+0.0001
2'.	35	= 0.2189	1.2	= 0.0012	0.0013	+0.0001
3'.	33	= 0.1867	2.0	= 0.0020	0.0019	-0.0001

Separation of Titanium from Iron.

As solutions of titanium chloride are quite unstable, a standard solution of the sulphate was prepared as follows:—Potassium titanio-fluoride of the market was twice crystallised from hot water and dried at 105° C. A weighed quantity of this compound was then heated in a large platinum crucible with excess of sulphuric acid until free from fluorine. A very low flame should be used, or insoluble basic sulphate may form. The cooled sulphate was then poured into excess of cold water, precipitated by ammonia, washed, and re-dissolved in a quantity of sulphuric acid 5 or 10 per cent in excess of that demanded by theory, to prevent hydrolysis.

Phenylhydrazine gives a practically complete separation of titanium from iron in two precipitations. I have never found more than traces of titanium remaining with the iron. It was sought for as follows:—The iron, with any titanium it might contain after the precipitation with phenylhydrazine, was removed from the solution by ammonium sulphide, washed a few times, and dissolved in nitric acid, from which solution it was subsequently precipitated by ammonia, and weighed. The weighed oxide was now tested for titanium by the method described in *Bulletin* 176, U.S. Geol. Survey, p. 67.

TiO ₂ found in Fe ₂ O ₃ .	I. ..	0.000017	410.
	II. ..	none	
	III. ..	0.0002	
	IV. ..	0.0002	
	V. ..	trace	

The same details apply to this separation as were laid down for the separation of aluminum from iron, except that here the solution may be considerably more acid before adding the phenylhydrazine. If much titanium is present, a considerable precipitate will form before the solution is completely neutralised by ammonia. When the neutral-point is reached, a half-dozen drops of 1:1 hydrochloric acid may be added. This quantity is frequently insufficient to re-dissolve all the titanium precipitate, but that is a matter of no consequence. (See Table A).

Separation of Zirconium from Iron.

A standard solution of zirconium sulphate was used in these experiments. The raw material consisted of picked crystals of North Carolina zircon,* which were converted into potassium zirconio-fluoride after the excellent method of Marignac (*Ann. Chim., Phys.*, [3], ix., 260).

After two crystallisations it was dried carefully at 105° C., and then changed into sulphate by a method similar in all details to that given for the titanium compound. 1.0470 gm. of the above preparation, thus treated and afterwards precipitated by ammonia, thoroughly washed, dissolved in hydrochloric acid, and again precipitated and washed as before, ignited, and finally blasted, gave 0.4508 gm. ZrO₂ instead of 0.4529 gm. required for K₂ZrF₆.

The details of the separation of zirconium from iron are the same as those for the separation of titanium. The results given in Table B. show that a single precipitation is not always sufficient to remove all the iron.

Separation of Aluminum, Titanium, and Zirconium from Iron.

In the series of determinations, given in Table C., aluminum, zirconium, and titanium in varying quantities were separated from iron as already described, and weighed together. The standard solutions used have already been described.

In a recent paper by Miss A. M. Jefferson (*Journ. Am. Chem. Soc.*, xiv., 543) it is stated that zirconium is not precipitated by phenylhydrazine. Now zirconia is certainly a weaker base than alumina, and, according to the principles stated in the beginning of this paper, ought to be precipitated by phenylhydrazine, the more so since, according to Miss Jefferson, it is precipitated by aniline, a base which my experiments indicate to be somewhat weaker than phenylhydrazine. It should be noted, however, that Miss Jefferson employed a cold solution of zirconium nitrate, while the experiments I have described were performed with solutions containing sulphates and chlorides, or chlorides alone. As theory indicates the possibility of a difference, the following tests were undertaken:—Zirconium hydroxide was prepared from the sulphate, and then dissolved in dilute nitric acid. The solution was freed from most of the acid by evaporating to a volume of a few c.c., and diluted with cold water so that 1 c.c. contained about 1 m.grm. ZrO₂. The solution contained no sulphate. In the first test, a portion of it was precipitated by a large excess of phenylhydrazine, 5 c.c. to 25 c.c. of the solution. After standing more than twenty-four hours, the precipitate was filtered, washed, ignited, and blasted.

	Found.	By ammonia.
ZrO ₂ =	0.0251	0.0245

Twenty-five c.c. of the solution with 1 c.c. of the reagent gave ZrO₂ = 0.0241 gm. Ammonia gave no precipitate with the filtrate. I could not discover that the zirconium

* From the *Journal of the American Chemical Society*, xxv., No. 4.

* My thanks are due to Mr. Wm. Taft, Assistant Curator of the National Museum, from whom the zircon, as well as a supply of beryl, was obtained.

TABLE A.

No.	FeCl ₃ taken. C.c.	Fe ₂ O ₃ . Grm.	Fe ₂ O ₃ found. Grm.	Error. Grm.	Ti(SO ₄) ₂ taken. C.c.	TiO ₂ . Grm.	TiO ₂ found. Grm.	Error. Grm.
1.	35	=	0.1748	—	2	=	0.0020	+0.0002
2.	5	=	0.0250	+0.0004	25	=	0.0246	-0.0009
3.	2	=	0.0100	+0.0004	25	=	0.0246	+0.0008
4.	25	=	0.1248	—	1	=	0.0010	+0.0001
5.	10	=	0.0499	—	50	=	0.0492	+0.0009
6.	3	=	0.0140	—	50	=	0.0492	+0.0010

TABLE B.

No.	FeCl ₃ taken. C.c.	Fe ₂ O ₃ . Grm.	Zr(SO ₄) ₂ taken. C.c.	TiO ₂ . Grm.	ZrO ₂ found. Grm.	Error. Grm.
Single Precipitation.						
1.	30	=	0.1876	2	=	0.0020
2.	4	=	0.0250	23	=	0.0229
3.	1	=	0.0062	25	=	0.0249
4.	35	=	0.2189	1	=	0.0010
5.	10	=	0.0625	50	=	0.0498
6.	1	=	0.0062	50	=	0.0498

Double Precipitation.

1.	50	=	0.2997	50	=	0.0500	-0.0004
2.	50	=	0.2997	1	=	0.0010	+0.0001
3.	5	=	0.0300	25	=	0.0249	-0.0002

TABLE C.

No.	Fe ₂ O ₃ taken. Grm.	Al ₂ O ₃ taken. Grm.	TiO ₂ taken. Grm.	ZrO ₂ taken. Grm.	Al ₂ O ₃ + TiO ₂ + ZrO ₂		Error. Grm.
					taken. Grm.	found. Grm.	
1.	0.0999	0.1500	0.00985	0.00492	0.1648	0.1654	+0.0006
2.	0.1249	0.1650	0.01477	0.00196	0.1817	0.1816	-0.0001
3.	0.1748	0.0500	0.0197	0.00287	0.0726	0.0717	-0.0009
4.	0.0749	0.1000	0.0049	0.00098	0.1059	0.1063	+0.0004
5.	0.1748	0.0250	0.0197	0.0148	0.0595	0.0603	+0.0008
Average					..	..	+0.00016

hydroxide had any tendency to dissolve in excess of phenylhydrazine. The same statement may be made of aniline, which also precipitates zirconium completely.

It was thought to be of some interest to determine the behaviour of phenylhydrazine with the remaining elements of this natural family, thorium and cerium.

Phenylhydrazine and Thorium.

A solution of thorium nitrate was prepared from the pure dioxide. The latter was brought into solution by fusion with potassium acid sulphate, from which it was precipitated by ammonia in a form soluble in dilute nitric acid. A double precipitation was necessary to remove sulphate entirely. The nitrate was evaporated to crystallisation, and dissolved in cold water.

Three portions of 25 c.c. each were then precipitated as follows:—No. 1 was precipitated by ammonia, washed, ignited, and weighed as in an ordinary determination. No. 2 was nearly neutralised with ammonia, precipitated hot, and washed with hot water. No. 3 was treated as No. 2, except that a smaller amount of reagent was added to the cold solution, and the precipitate was washed with cold water. In all cases the precipitate was blasted before weighing.

ThO₂ found.

- 25 c.c. contained 0.0477 grm. average of three determinations by NH₃.
- 25 c.c. hot by phenylhydrazine 0.0477 grm.
- 25 c.c. cold by phenylhydrazine 0.0475.

The precipitated thorium was white or nearly so.

Regarding Miss Jefferson's statement (*Yourn. Am. Chem. Soc.*, xxiv., 546) that phenylhydrazine throws down, from a solution of thorium nitrate, "a canary-yellow precipitate,

easily soluble in excess," I can say that if the solution contains much free nitric acid, the precipitate is coloured yellow, evidently by an oxidation product of the phenylhydrazine. The precipitate may be obscured by an excess of reagent, but there is no tendency to re-dissolve. Thus, in one test I employed 5 c.c. of the reagent to a small volume of the thorium solution. I was at first in doubt about the result, but a careful examination showed that no thorium passed through an ordinary filter.

Phenylhydrazine and Cerium.

The remaining element in the family under consideration is cerium. It differs from the other three members, in that it is easily reducible from the quadrivalent to the trivalent state. Phenylhydrazine fails to precipitate it except in a partial way from its ceric salts, not because it is a more basic element than the rest, but because it is an oxidising agent which phenylhydrazine easily reduces to the cerous condition, and cerous oxide is a much stronger base. These statements were proved by the following experiments:—

Ceric ammonium nitrate, (NH₄)₂Ce(NO₃)₆·14H₂O, was made from a preparation of cerous nitrate furnished by Merck. To separate it from any neodymium and praseodymium, it was twice precipitated by caustic potash and oxidised by a stream of chlorine, the ceric hydroxide being thoroughly washed after each treatment. The ceric hydroxide was now changed to ceric ammonium nitrate by the addition of dilute nitric acid and a little ammonium nitrate. A comparatively concentrated solution of this salt, containing considerable free acid, at once oxidised both phenylhydrazine and aniline with marked colour changes, and no excess of either produced, thereafter, any precipitate (see also "Gmelin-Kraut," vol. ii., Part I., p.

508). With a dilute and nearly neutral solution, the results were different. Such a solution was obtained by evaporating one like the above to dryness in a vacuum desiccator with lime and sulphuric acid.

The beautiful orange crystals, with the small excess of ammonium nitrate they contained, were then put into solution by cold water, and after standing a day or two, filtered from a slight precipitate which had formed. The concentration of this solution was not far from 1 m.-gm. CeO_2 per c.c. (20 c.c. gave 0.0161 gm.). Fifteen c.c. of the solution were treated with a little phenylhydrazine and set away for twenty-four hours. Some little precipitate, composed partly of organic matter, apparently an oxidation product of the reagent, had formed, but the filtrate yielded with ammonia 0.0078 gm. CeO_2 out of a total quantity of 0.0121 gm. originally contained in the solution. Aniline being a weaker reducing agent gave a practically complete precipitation with this solution. Only two or three very small flakes were obtained from the filtrate by ammonia.

Phenylhydrazine and Ferric Salts.

Ferric salts follow ceric salts in their behaviour, except that phenylhydrazine gives with the former almost no precipitate. This is true, at least, with both strong and weak solutions of ferric chloride. With one containing about 1 m.-gm. per c.c., phenylhydrazine at first brings down some brown hydroxide, which dissolves when the liquid is shaken, leaving only a little insoluble tarry matter. Aniline, however, gives a complete precipitation; at least the filtrate is colourless, and gives no precipitate with ammonia.

(To be continued).

THE POSITION OF CHEMISTRY IN THE MEDICAL CURRICULUM OF THE UNIVERSITY OF LONDON.

A.—RESOLUTIONS ADOPTED BY THE RECOGNISED TEACHERS OF CHEMISTRY IN MEDICAL SCHOOLS OF LONDON, DECEMBER 5TH, 1903.

(Submitted to the Academic Council of the University).

In view of the changes in the character of the requirements relating to the teaching of chemistry for medical degrees of the London University, at a meeting of the recognised teachers of chemistry at medical schools the following resolutions were unanimously passed:—

1. That instruction in physiological and pathological chemistry can in no sense be regarded as taking the place of instruction in the pure scientific organic chemistry hitherto required by the University.
2. That this instruction in organic chemistry can only properly be given in a chemical laboratory and by a chemist.
3. That a careful scientific study of organic chemistry is essential for any later intelligent study of physiological and pathological chemistry.
4. That this study of organic chemistry must be preceded by a study of inorganic chemistry.
5. That to properly carry out such an education the Preliminary Scientific Examination in chemistry might be made identical with the present Intermediate Science Examination for internal students; and that to provide for the proper study of organic chemistry necessary a further period is required.
6. That to relieve the student the examination should be in two parts:—(1) Inorganic chemistry identical with the present Intermediate Science Examination for internal students, and (2) an examination in organic chemistry, held at convenient times.
7. That in the opinion of the teachers of chemistry it would be possible for a student to take the examination in both inorganic and organic chemistry at

the end of one academic year, only when he has taken chemistry at the Matriculation Examination.

8. That it is desirable that a more detailed syllabus in chemistry for the Preliminary Scientific Examination for internal students be prepared.

In the event of the University favouring the above suggestions, the teachers of chemistry in the medical schools of the University would be prepared to submit a schedule for consideration by the Board of Studies in Chemistry.

These resolutions were supported by the University Professor of Chemistry, and the Lecturers on Chemistry in the Medical Schools of the University:—

Hugh Candy, B.A., B.Sc.; F. D. Chattaway, M.A., D.Sc., Ph.D.; Arthur W. Crossley, D.Sc.; Clare de B. Evans, D.Sc.; J. Addyman Gardner, M.A.; H. Wilson Hake, Ph.D.; A. M. Kellas, B.Sc., Ph.D.; H. Forster Morley, M.A., D.Sc.; Frederic J. M. Page, B.Sc.; Sir W. Ramsay, Sc.D., F.R.S.; John M. Thomson, LL.D., F.R.S.; John Wade, D.Sc.; W. H. Willcox, M.D., B.Sc.

B.—RECOMMENDATIONS OF THE RECOGNISED TEACHERS OF CHEMISTRY IN MEDICAL SCHOOLS OF LONDON.

(Drawn up at the Request of the Vice-Chancellor of the University).

December 22nd, 1903.

In view of the changes in the character of the regulations relating to the teaching of chemistry for medical degrees of the University of London, the following resolutions have been approved by the undersigned, being the recognised teachers of chemistry in the twelve medical schools of the University. They believe that these recommendations can be carried into effect without lengthening the medical course.

1. That instruction in physiological and pathological chemistry can in no sense be regarded as taking the place of instruction in the pure scientific organic chemistry hitherto required by the University.
2. That this instruction in organic chemistry can only properly be given in a chemical laboratory and by a chemist.
3. That a careful scientific study of organic chemistry is essential for any later intelligent study of physiological and pathological chemistry.
4. That this study of organic chemistry must be preceded by a study of inorganic chemistry.
5. That to properly carry out such an education the Preliminary Scientific Course and Examination in Chemistry should be identical in scope with the revised Intermediate Course and Examination in Science.
6. That to provide for the proper study of organic chemistry a further period is required followed by a University examination conducted by chemists.
7. That the examination in organic chemistry should consist of a three hours' paper and three hours' practical work.
8. That it would be impossible for a student to take the examination in both inorganic and organic chemistry at the end of one academic year, unless he had previously studied inorganic chemistry.

As an indication of the amount of organic chemistry necessary, the teachers of chemistry in the medical schools of the University are prepared to submit a draft schedule adapted to medical requirements:—

Edward C. Cyril Baly (University), Hugh Candy (London), F. D. Chattaway (St. Bartholomew's), Arthur W. Crossley (St. Thomas's), Clare de B. Evans (Royal Free), J. Addyman Gardner (St. George's), H. Wilson Hake (Westminster), A. M. Kellas (Middlesex), H. Forster Morley (Charing Cross), John M. Thomson (King's), John Wade (Guy's), W. H. Willcox (St. Mary's).

C.—MEMORANDUM ON THE POSITION OF CHEMISTRY IN THE MEDICAL CURRICULUM.

(Being a Reply to the Recent Report of the Board of Intermediate Medical Studies of the University of London).

The recent changes in the regulations relating to the medical degrees of the University of London, whereby the study of Organic Chemistry has been relegated to the preliminary scientific year, and must therefore be taken concurrently with Inorganic and General Chemistry, Experimental Physics, and General Biology, render it impossible for the student to acquire that knowledge of the scientific chemical basis of Physiology and Pathology, which has hitherto been ensured by the inclusion of Organic Chemistry in the Intermediate Examination in Medicine.

The reasons for thus lowering the standard of scientific medical education appear to be summarised in a report which has recently been formulated by the Board of Intermediate Medical Studies (October 27th, 1903), from which the following excerpt is taken:—

"This Board is strongly of opinion that the student of Medicine should complete his study of Pure Chemistry before beginning Anatomy and Physiology. Hitherto the study of these fundamental medical sciences has been hampered and injuriously limited by the amount of time, always considerable and of late years increasing, necessarily devoted to Organic Chemistry. Nevertheless, that subject has always offered great difficulties to the student, and it is within the knowledge of many teachers that rejections in Chemistry at the Intermediate Examination in Medicine have commonly been more numerous than in either Anatomy or Physiology. The subject of Chemistry has overweighted the Intermediate Examination, and has been a great obstacle to the attainment of the Degree of the University. This Board is therefore resolutely opposed to the reinstatement of Chemistry in the Intermediate Course.

"It is further to be observed that, under the existing arrangement, the study of Chemistry by the student of Medicine does not cease with the Preliminary Scientific Examination. The application of Chemistry to Biological phenomena and processes forms a large part of the subjects of Physiology and Pathology. The special branches of Physiological Chemistry in the Intermediate Course and of Pathological Chemistry in the Advanced Course have now been greatly extended, and much practical work in these subjects has been introduced. In this way the student will obtain his training in Medical Chemistry; and he is no longer dependent on the Course of Pure Chemistry alone for his education in this subject. The position occupied by Pure Chemistry in the present medical curriculum is entirely that of a Preliminary Scientific study, and in no sense a Professional Study. What is required from the pure Chemist for medical students is, not to make them Organic Chemists, but to give them such an elementary grounding in Chemistry that they may be able to enter upon the study of the special branches of Physiological and Pathological Chemistry.

"Under these circumstances this Board is of opinion that there should be no difficulty in including the required amount of Chemistry, together with the other subjects, in the one year's Preliminary Scientific work, and that the Preliminary Scientific Examination, in respect of Chemistry, should be put on the same level with the Intermediate Examination in Science."

It is noteworthy, however, that when this report came before the Faculty of Medicine (December 11th, 1903), it was "received" but not adopted, and it was resolved by this body, after careful consideration, "that while agreeing that the Student of Medicine should complete his study of Pure Chemistry before beginning Anatomy and Physiology, the Faculty is of opinion that one year is insufficient for its proper study."

In discussing the position of Chemistry in the Medical curriculum, no one at the present day who is conversant

with modern Physiology and Pathology can fail to realise that the association of Chemistry, and especially of Organic Chemistry, with these subjects is constantly becoming closer; the Board of Intermediate Studies does not indeed deny this. An advanced knowledge of Pure Organic Chemistry of a special type is essential for the intelligent pursuit of Physiology and Pathology, and it is to be presumed that it is seriously proposed by this Board that instruction in this necessary Organic Chemistry should form part of the Physiological Course. It is, however, impossible for a teacher who is engaged in Physiological research to remain familiar with the difficulties encountered by the student of Organic Chemistry; for although the Physiologist during his studentship has become acquainted with the fundamental facts of this Science, he cannot possibly retain that intimacy with them which comes as a matter of course to the Chemist.

The Advanced Organic Chemistry on which Physiology is based, and which has hitherto been studied by the Intermediate student in Medicine, differs widely from a course which would be suited to the requirements of students of Pure Chemistry. Numerous sections of great Chemical interest, covering a vast extent of ground, such as the coal-tar dyes, and the derivatives of naphthalene and anthracene, are entirely omitted, as having no immediate bearing on Physiology and Pathology, whilst other sections, such as the Chemistry of the nitrogen compounds and carbohydrates, are needed to an extent which would not be warranted by their purely Chemical interest. It is not correct, therefore, to say that the Organic Chemistry taught under the former regulations as part of the Intermediate Course in Medicine was in no sense a professional study; it was essentially professional in character, and would not have suited any but medical students.

Organic Chemistry is based on Inorganic Chemistry, and cannot be taught to students having no previous knowledge of this division of the subject; hence the teaching of the two branches cannot be included in one academic year, if it is to be of University standard. Even when a University standard is not demanded, it is recognised that no more than the rudiments of Organic Chemistry can be taught together with Inorganic Chemistry during this period. In their recent Report on the various "qualifying" medical examinations, the Visitors of the General Medical Council, after dwelling on "the great and growing importance in Medicine of an acquaintance with the carbon compounds," remark that "the subject is so large, that only the outer fringe of it can be touched in the first year of medical study."

Organic Chemistry most emphatically has not "over-weighted the Intermediate Examination," nor "been a great obstacle to the attainment of the degree of the University," as the Board of Intermediate Studies maintains; at some of the largest of the London medical schools, where a record has been kept, the rejections have not been greater than those in Anatomy and Physiology, but such as might reasonably be expected where students are allowed to present themselves without selection. Not only is the subject not detrimental, but it constitutes in the opinion of most authorities a valuable complement in training to the study of the other Intermediate subjects.

It has been stated that sufficient Organic Chemistry for Medical students is included in the Intermediate Examination in Science. The amount in this syllabus, however, is merely nominal, and quite inadequate as a foundation for Physiological Chemistry. Hence the Intermediate Examination in Science should not be accepted as at present, as exempting the Medical student from the further study of Organic Chemistry. The former Preliminary Scientific Examination was substantially identical with the present Intermediate Examination in Science, and contained quite as much Chemistry as could be assimilated in an academic year by a student having to devote two-thirds of his time to Physics and Biology; there appears to be no reason why the two examinations should not again become

identical, as the Board of Intermediate Studies proposes, so far as Inorganic Chemistry is concerned.

It has been suggested that the Chemistry of the Matriculation Examination might be accepted in place of the Inorganic Chemistry of the Preliminary Scientific Examination. A Matriculation Course, however, should aim rather at the inculcation of scientific method, than at teaching the essential facts of Chemistry, and can in no sense be regarded as equivalent to the systematic study and Laboratory work required for the Preliminary Scientific Examination.

As more than one year is necessary—and this is the opinion not only of the Chemists and many Physiologists, but also of the Faculty of Medicine—it follows that if the student is to complete his study of Chemistry before beginning the two years' course of Anatomy and Physiology, the curriculum will extend over more than five years from Matriculation. There is, however, no sufficient reason why the study of Organic Chemistry should not, as formerly, run concurrently with that of Anatomy and Physiology during the first year of Intermediate studies. The Preliminary Scientific year is hopelessly overweighted by the recent regulations, and such students as may pass the examination in one year under present conditions will have no real grasp of their work; it is impossible for any student, however capable, without a previous knowledge of Chemistry to work through the present syllabus under eighteen months.

If, however, the Preliminary Scientific Examination were made identical with the Intermediate Examination in Science, it could be passed easily after one year's study; and if a subsequent special course in Organic Chemistry were arranged, forming as far as possible an introduction to Physiological and Pathological Chemistry, and followed by a University Examination, the standard would be maintained without lengthening the curriculum or overburdening the students. This Examination could be held at the same times as the Intermediate Examination in Medicine, but candidates, instead of being compelled to wait two years as under the former regulations, might be allowed to present themselves for it at any time after passing in the Chemistry of the Preliminary Scientific Examination or Intermediate Examination in Science.

P. Phillips Bedson (Newcastle), Hugh Candy (London), F. D. Chattaway (St. Bartholomew's), Arthur W. Crossley (St. Thomas's), Clare de B. Evans (Royal Free), Percy F. Frankland (Birmingham), J. Addyman Gardner (St. George's), H. Wilson Hake (Westminster), A. M. Kellas (Middlesex), H. Forster Morley (Charing Cross), John M. Thomson (King's), John Wade (Guy's), W. H. Willcox (St. Mary's), W. Carleton Williams (Sheffield).

January 11th, 1904.

D.—COPY OF THE ORIGINAL MEMORIAL ADDRESSED TO THE VICE-CHANCELLOR IN 1901, WHEN THE CHANGES WERE IN CONTEMPLATION.

WE, the undersigned Teachers of Chemistry in the University of London, and others interested in Medical Education, having heard that proposals to exclude Organic Chemistry from its present position in the Medical curriculum, or to exclude it entirely in favour of Chemical Physiology, are to be brought before the Senate, beg leave to represent—

1. That the resolution to exclude Organic Chemistry from the Intermediate M.B. Examination was arrived at by a Board of eleven members, of whom only one represented Chemistry, and he was opposed to the resolution arrived at.

2. That the exclusion of Organic Chemistry, as taught by recognised teachers of Chemistry, from the curriculum of the medical student would be a retrograde step, would involve a lowering of the value of the London Degree, and would be contrary to the practice of other Universities. Chemical Physiology cannot be taught without a previous knowledge of Organic Chemistry.

3. That it is impossible to include Organic Chemistry, which is a necessary introduction to Physiology and Pathology, in the course of chemical teaching given for the Preliminary Scientific Examination.

4. That it is impossible to insure that a competent knowledge of Inorganic Chemistry can be acquired at the stage at which a candidate matriculates.

5. That the subject of Organic Chemistry should be retained in the Intermediate M.B. Examination, and that the Examination in this subject be taken at the end of the year following that in which the Preliminary Scientific Examination is passed.

6. That this compromise secures that the subject of Organic Chemistry will occupy only part of one year of the Medical curriculum, instead of two, as at present, and that Elementary Anatomy or Physiology can be studied concurrently with Organic Chemistry.

This Memorial was signed by—

Prof. Clifford Allbutt, F.R.S.; Prof. H. E. Armstrong, F.R.S.; Dr. Buckmaster; Mr. Hugh Candy; Dr. A. W. Crossley; Prof. Wyndham Dunstan, F.R.S.; Prof. Percy Frankland, F.R.S.; Mr. Addyman Gardner; Prof. Francis Gotch, F.R.S.; Mr. C. E. Groves, F.R.S.; Dr. Wilson Hake; Dr. A. M. Kellas; Prof. Liveing, F.R.S.; Dr. Moore; Dr. Forster Morley; Prof. Odling, F.R.S.; Mr. F. J. M. Page; Dr. Phillips, F.R.S.E.; Prof. W. Ramsay, F.R.S.; Prof. Emerson Reynolds, F.R.S.; Dr. W. J. Russell, F.R.S.; Mr. Chas. Slater; Dr. Thos. Stevenson; Prof. W. A. Tilden, F.R.S.; Prof. J. M. Thomson, F.R.S.; Mr. John Wade; Mr. W. H. Willcox; Prof. Carleton Williams; Dr. George Young.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, January 20th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. U. O. S. Nairne and J. T. Hall were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. J. P. Ackroyd, B.Sc., 116, Richmond Street, Accrington, Lancs.; Charles Thomas Bennett, 57, Larkhall Rise, Clapham, S.W.; George E. P. Broderick, B.Sc., Lampeter, South Wales; Julian Drugman, Ph.D., La Bocca, Cannes, France; George Fry, Carlin Brae, Berwick-on-Tweed; Francis D'Oyley Messers, jun., 4, Nyanza Terrace, Swansea; Jatindranath Sen, M.A., 71, Cathedral Mission Lane, Calcutta; Raymond Louis Siau, 15, Merridale Lane, Wolverhampton; Henry E. Stevenson, Avondale, Ditton Hill, Surrey; Charles H. Thompson, Hillcroft, Ambleside, Stourbridge; Hubert Thompson, B.Sc., Holmes Chapel, Cheshire; Léon Edward Walling, 43, Union Road, Rotherhithe; Charles Edward Whiteley, 9, Abyssinia Grove, Leeds; William Henry Woodcock, 10, Chesson Road, West Kensington, W.

Certificates in favour of the following were authorised by the Council for presentation for ballot under By-law I. (3):—Anu Ghose, 42, Shambazar Street, Calcutta; J. P. Montgomery, Agricultural College, Starkville, Miss., U.S.A.

The President announced that since the last meeting of the Society the Rev. T. J. Prout, M.A., F.G.S., Senior Student of Christ Church, Oxford, had presented to the Society a photograph of a portrait by Hayes of his father, Dr. William Prout, F.R.S., which was considered to be a very good likeness of the author of the famous paper "On the Relation between the Specific Gravities of Bodies in

their Gaseous State and the Weights of their Atoms," published anonymously in Thomson's *Annals of Philosophy* in November, 1815.

The Council has ordered the following report to be printed in the Journal and in the Proceedings of the Society:—

REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

The International Committee on Atomic Weights* has the honour to offer the following report:—

In the table of atomic weights for 1904, only two changes from 1903 are recommended. The atomic weight of caesium has been slightly modified to accord with the recent determinations by Richards and Archibald, and that of cerium in conformity with the measurements by Brauner. The value for lanthanum is still in controversy, and any change here would therefore be premature. The same consideration may also be urged with regard to iodine. Ladenburg has shown that the accepted number for iodine is probably too low, but other investigations upon the subject are known to be in progress, and until they have been completed it would be unwise to propose any alteration.

International Atomic Weights. (1904)

		O=16.	H=1
Aluminium	Al	27.1	26.9
Antimony	Sb	120.2	119.3
Argon	A	39.9	39.6
Arsenic	As	75.0	74.4
Barium	Ba	137.4	136.4
Bismuth	Bi	208.5	206.9
Boron	B	11	10.9
Bromine	Br	79.96	79.36
Cadmium	Cd	112.4	111.6
Cæsium	Cs	132.9	131.9
Calcium	Ca	40.1	39.8
Carbon	C	12.00	11.91
Cerium	Ce	140.25	139.2
Chlorine	Cl	35.45	35.18
Chromium	Cr	52.1	51.7
Cobalt	Co	59.0	58.56
Columbium	Cb	94	93.3
Copper	Cu	63.6	63.1
Erbium	Er	166	164.8
Fluorine	F	19	18.9
Gadolinium	Gd	156	155
Gallium	Ga	70	69.5
Germanium	Ge	72.5	71.9
Glucium	Gl	9.1	9.03
Gold	Au	197.2	195.7
Helium	He	4	4
Hydrogen	H	1.008	1.000
Indium	In	114	113.1
Iodine	I	126.85	125.90
Iridium	Ir	193.0	191.5
Iron	Fe	55.9	55.5
Krypton	Kr	81.8	81.2
Lanthanum	La	138.9	137.9
Lead	Pb	206.9	205.35
Lithium	Li	7.03	6.98
Magnesium	Mg	24.36	24.18
Manganese	Mn	55.0	54.6
Mercury	Hg	200.0	198.5
Molybdenum	Mo	96.0	95.3
Neodymium	Nd	143.6	142.5
Neon	Ne	20	19.9
Nickel	Ni	58.7	58.3
Nitrogen	N	14.04	13.93
Osmium	Os	191	189.6
Oxygen	O	16.00	15.88
Palladium	Pd	106.5	105.7

Phosphorus	P	O=16.	H=1.
Platinum	Pt	194.8	193.3
Potassium	K	39.15	38.86
Praseodymium	Pr	140.5	139.4
Radium	Rd	225	223.3
Rhodium	Rh	103.0	102.2
Rubidium	Rb	85.4	84.8
Ruthenium	Ru	101.7	101.0
Samarium	Sm	150	148.0
Scandium	Sc	44.1	43.8
Selenium	Se	79.2	78.6
Silicon	Si	28.4	28.2
Silver	Ag	107.93	107.12
Sodium	Na	23.03	22.88
Strontium	Sr	87.6	86.94
Sulphur	S	32.06	31.83
Tantalum	Ta	183	181.6
Tellurium	Te	127.6	126.6
Terbium	Tb	160	158.8
Thallium	Tl	204.1	202.6
Thorium	Th	232.5	230.8
Thulium	Tm	171	169.7
Tin	Sn	119.0	118.1
Titanium	Ti	48.1	47.7
Tungsten	W	184.0	182.6
Uranium	U	238.5	236.7
Vanadium	V	51.2	50.8
Xenon	Xe	128	127
Ytterbium	Yb	173.0	171.7
Yttrium	Yt	89.0	88.3
Zinc	Zn	65.4	64.9
Zirconium	Zr	90.6	89.9

Many of the atomic weights given in the table are well known to be more or less uncertain. This is especially true with respect to the rarer elements, such as gallium, indium, columbium, tantalum, &c. But some of the commoner elements also stand in need of revision, and we venture to call attention to a few of these. Among the metals, the atomic weights of mercury, tin, bismuth, and antimony should be re-determined, for the reason that the existing data are not sufficiently concordant. Palladium also, on account of discrepancies between different observers, and possibly vanadium, for which the data are too few, deserve some attention. Among the non-metals, phosphorus has been peculiarly neglected, and our knowledge of the atomic weight of silicon rests upon a single ratio. In the latter case, confirmatory data are much to be desired. Upon any of these elements, new investigations would be most serviceable.

There is one other point to which we may properly call attention. Many of the ratios from which atomic weights have been calculated were measured in vessels of glass, by processes involving the use of strong acids. In such cases, the solubility of the glass becomes an important consideration, even when no transfer of material from one vessel to another has occurred. A slight conversion of silicate into chloride would cause an increase of weight during the operation, and so introduce an error into the determination. Such errors are doubtless very small, but still they ought not to be neglected. Now that vessels of pure silica, the so-called quartz-glass, are available for use, they might well replace ordinary glass in all processes for the determination of atomic weights. An investigation into the relative availability of the two kinds of glass is most desirable.

F. W. CLARKE
T. E. THORPE
K. SEUBERT
HENRI MOISSAN } Committee.

Of the following papers, those marked * were read:—

*1. "The Chemical Reactions of Nickel Carbonyl. Part I. Reactions with the Halogens and other Inorganic Substances." By JAMES DEWAR and HUMPHREY OWEN JONES.

* The original members of the Committee take great pleasure in announcing the addition to their number of Professor Henri Moissan. They are confident that this increase will meet with universal approval.

The previous study of the physical properties of nickel carbonyl (*Proc. Roy. Soc.*, 1903, 181, 627) showed that it was a comparatively stable substance when heated under pressure. The authors have undertaken the investigation of its chemical behaviour mainly from a thermochemical standpoint, with the view of studying its constitution and its possible use as a synthetic agent.

Nickel carbonyl is completely decomposed by solutions of chlorine, bromine, iodine, cyanogen, and sulphur in organic solvents, carbon monoxide and a nickel compound being produced; in no case was any combination of the carbon monoxide with the halogen or other reagent observed, even when a considerable excess of the latter was present.

From Mittasch's value (52.2 Cal.) for the heat of formation of nickel carbonyl and Thomsen's values for nickel compounds, it was to be expected that chlorine and bromine would decompose it readily, but that iodine, cyanogen, and sulphur would not. In the case of iodine, the heat necessary to carry out the reaction appears to be obtained by the formation of molecular complexes of nickel iodide and the solvent (for example, ether and chloroform), and in the case of sulphur by the formation of a higher sulphide, probably Ni_2S_3 . Liquid chlorine and bromine decompose solid nickel carbonyl, but solid iodine appears to have no action on liquid nickel carbonyl.

Iodine mono- and tri-chlorides and cyanogen iodide in carbon tetrachloride solution react with nickel carbonyl in two distinct stages, the free iodine liberated at first subsequently decomposing a further quantity of nickel carbonyl.

Hydrogen iodide readily interacts with nickel carbonyl, whereas the corresponding bromide and chloride do not affect it.

Hydrogen sulphide reacts very slowly with nickel carbonyl, producing nickel monosulphide, hydrogen and carbon monoxide. Sulphuric acid also decomposes the compound slowly, giving rise to nickel sulphate, hydrogen, and carbon monoxide.

*2. "The Chemical Reactions of Nickel Carbonyl. Part II. Reaction with Aromatic Hydrocarbons in Presence of Aluminium Chloride. Synthesis of Aldehydes and Anthracene Derivatives." By JAMES DEWAR and HUMPHREY OWEN JONES.

Nickel carbonyl does not react with either aluminium chloride or benzene separately, but with a mixture of the two substances a violent reaction begins immediately and torrents of hydrochloric acid are evolved. The reaction with various benzene homologues has been investigated both at the ordinary temperature and also at 100° .

From benzene at the ordinary temperature, benzaldehyde is produced together with traces of oils having high boiling points. At 100° , the quantity of benzaldehyde is much smaller, and anthracene, which is now the chief product, is produced in considerable quantities. The mechanism of this production of anthracene from benzaldehyde has not been elucidated, but the reduction is probably due to the action of the nickel produced by the decomposition of the nickel carbonyl.

Toluene gives β -tolualdehyde and 2:6-dimethylanthracene (m. p. $215-216^\circ$). *m*-Xylene similarly yields 2:4-dimethylbenzaldehyde and a tetramethylanthracene melting at 280° , which is in all probability 1:3:5:7 tetramethylanthracene. Mesitylene yields an aldehyde only, condensation to an anthracene derivative being in this case impossible.

Naphthalene behaves in an entirely different way; no aldehyde is formed either in the cold or at 100° , and a hydrocarbon, $\text{C}_{16}\text{H}_{12}$, is produced together with oily or resinous substances having very high boiling points, which appear to be further condensation products, since the quantity produced is much greater at the higher temperature. This hydrocarbon, which melts at $180-181^\circ$, is probably identical with that obtained by Bischoff by the

interaction of naphthalene and methyl chloride in the presence of aluminium chloride, and may also be identical with that produced from ruficoccine or coccine by distillation with zinc dust.

*3. "Optically Active Asymmetric Nitrogen Compounds. d- and l-Phenylbenzylmethylallyl ammonium Salts." By HUMPHREY OWEN JONES.

The resolution of the phenylbenzylmethylallyl ammonium salts was undertaken with the view of showing that optical activity in nitrogen compounds was independent of the existence of isomerides of the compound in question.

The only optically active nitrogen compounds known at present are the *d*- and *l*-phenylbenzylmethylallyl ammonium salts, and these are also the only quinquivalent nitrogen compounds (not containing an asymmetric carbon atom) which have been shown to exist in definite stable isomeric forms.

Phenylbenzylmethylallyl ammonium iodide has been prepared in the three possible ways, namely, by the following combinations:—(1) methylallylaniline and benzyl iodide, (2) benzylallylaniline and methyl iodide, (3) benzylmethylallylaniline and ethyl iodide. The velocity of formation of the iodide is remarkably different in the three cases, that in the first combination being the greatest and that in the third being the least. The compound produced, which is the same in all three cases, crystallises from alcohol in lustrous, prismatic prisms, the melting point of which is about $140-142^\circ$, but this is to a certain extent dependent on the rate of heating.

The iodide was converted into the *d*- and *l*-camphorsulphonates by boiling molecular proportions of the salt and silver *d*- and *l*-camphorsulphonates with ethyl acetate and a small quantity of alcohol.

The camphorsulphonate was crystallised repeatedly from a mixture of dry ethyl acetate and ethylal at a comparatively low temperature until its rotatory power was constant. *d*-Phenylbenzylmethylallyl ammonium *d*-camphorsulphonate crystallises in lustrous prisms melting at $180-181^\circ$. It is very sparingly soluble in ethyl acetate and acetone and has $[\text{M}]_D = 71.0^\circ$ in aqueous solution.

The corresponding *l*-salt is identical with its *dd*-isomeride in appearance and properties and has $[\text{M}]_D = -71.2^\circ$. *d*-Phenylbenzylmethylallyl ammonium iodide, which was obtained by mixing the calculated quantities of potassium iodide and the *d*-camphorsulphonate in aqueous solution, has the same appearance, crystalline form, and melting point as the inactive iodide; it is very sparingly soluble in alcohol and other solvents. Its rotatory power is small, so that determinations of this constant are difficult, the observed $[\text{M}]_D$ being about 30° . The corresponding *l*-iodide, which was prepared from the *l*-camphorsulphonate in a similar manner, had $[\text{M}]_D = 30^\circ$ (approximately). The iodides undergo racemisation in chloroform solution, but their molecular weight in this solvent appears to be nearly normal at the ordinary temperature.

The inactive and laboratory bromides were also prepared and were found to melt at $155-156^\circ$. The latter compound has a higher specific rotatory power than the *l*-iodide.

The feeble rotatory power of these salts compared with that of the active α -phenylbenzylmethylallyl ammonium is remarkable, since the only difference is the replacement of an allyl by an ethyl radicle.

*4. "A Microscopic Method of Determining Molecular Weights." By GEORGE BARGER.

The author has continued the experiments of which a preliminary account has already been given (*Proc.*, 1903, xix., 121). The method is based on the comparison of the vapour pressures of two solutions, of which biconcave, lenticular drops are placed in a capillary tube. A difference in the vapour pressures causes a mutual variation in the size of the drops, which is observed by means of an eyepiece micrometer.

About one hundred determinations with various substances in eleven different solvents have now been made, and the experimental error is found to vary from 5 to 10 per cent. Solvents of widely differing boiling points have been employed, including ether, xylene, and light petroleum (b. p. 50–60°). Some determinations were performed with minute quantities of the dissolved substance.

The method is being applied to the study of association in mixtures of associative and non-associative solvents. The behaviour of benzoic acid in mixtures of benzene and ethyl alcohol, and of cinnamic acid in mixtures of chloroform and methyl alcohol, has so far been studied, the results showing that a small proportion of the alcohol suffices to give these acids a normal molecular weight. Should this phenomenon prove to be general, it would be of practical value in determining molecular weights in those cases where associative solvents only can be employed.

DISCUSSION.

Dr. PHILIP asked whether it would be possible to carry out the experiments at a higher temperature, nearer the boiling point of the solvent, in order to shorten the time necessary for the establishment of equilibrium between the drops.

Dr. HEWITT suggested the possibility of using two graduated tubes fitted with tightly-fitting india-rubber stoppers and connected by a T-tube, the third branch of which should have a stop-cock. Into one of the graduated tubes a standard solution could be introduced, and into the other a weighed quantity of the substance, together with some of the solvent. It would then only be necessary to exhaust the apparatus, place it in a bath until equilibrium was attained, allow to cool, and measure the respective volumes of solution in the two graduated tubes.

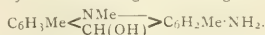
Mr. BARGER, in reply to Dr. Philip, said that the tubes must either be measured at the higher temperature or cooled down to that of the microscope. In the latter case, the solvent condenses between the drops on the walls of the tube, and thus produces an error. In the former case, it has not been found possible to prevent the condensation of water vapour on the frontal lens of the microscope objective.

Macroscopic methods similar to that suggested by Dr. Hewitt have been tried, both volumetrically and gravimetrically, but without the least success. The essential conditions which make the present method possible are.—

- (1) The accuracy with which extremely small changes in volume of the drops can be detected under the microscope.
- (2) The large evaporating surface presented by the drops, as compared with their volume.

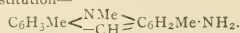
*5. "Studies in the Acridine Series." Part I. By JOHN JACOB FOX and JOHN THEODORE HEWITT.

The authors find that 6-acetamino-2:7-dimethylacridine (m. p. 270° uncorr., Ullmann gives 258°, *Ber.*, 1903, xxxvi., 1025) unites with methyl iodide to form a quaternary acridinium iodide, a substance yielding a precipitate with ammonia. The isolation of the corresponding carbinol seems impracticable on account of the ease with which the acetyl group is hydrolysed. To ensure complete hydrolysis, the solution obtained on boiling the precipitate with dilute sulphuric acid is treated with ammonia, when the base is liberated. This compound, which, when crystallised from acetone, has a pale red colour, melts at 210° (uncorr.) and corresponds with the formula $C_{16}H_{18}ON_2$; it is probably a carbinol having the following constitution:—

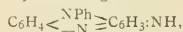


When the carbinol base is heated for some hours at 184°, partial dehydration occurs, and on warming the nitrobenzene solution of the substance, a very appreciable evolution of water is observed. On filtering the hot

solution and subsequently treating the cooled filtrate with light petroleum, a dark red compound, $C_{16}H_{14}N_2$, is deposited, which is readily soluble in acids and probably has the constitution—



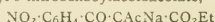
because the oxygen removed as water was attached in the carbinol base to the carbon atom of the median ring. Such a formula for the anhydro-base agrees with the constitution—



for the base of aposafranin, and does not correspond with the aposafranin formula suggested by Kehrman (com. *par. Ber.*, 1896, xxix., 2316; *Annalen*, 1896, ccxc., 256).

6. "o-Nitrobenzoylactic Acid." By EDWARD RUSHTON NEEDHAM and WILLIAM HENRY PERKIN, jun.

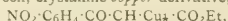
Ethyl sodioacetate (2 mols.) reacts readily with o-nitrobenzoyl chloride (1 mol.), yielding the sodium compound of ethyl o-nitrobenzoylacetate,



(Gevekoth, *Annalen*, 1883, ccxxi., 323), and when this product is digested with ammonia and ammonium chloride (compare Claisen, *Annalen*, 1896, ccxc., 67) the acetyl group is eliminated and ethyl o-nitrobenzoylacetate,



is produced. This ester is a pale brown oil which, in alcoholic solution, gives an orange-red colouration with ferric chloride; it readily dissolves in dilute aqueous caustic potash, yielding a yellow, crystalline, potassium derivative, $NO_2 \cdot C_6H_4 \cdot CO \cdot CHK \cdot CO_2Et$, and when its ethereal solution is shaken with ammoniacal copper sulphate, the green, crystalline copper derivative,



is obtained. Ethyl o-nitrobenzoylacetate dissolves in concentrated sulphuric acid, and if the solution is heated at 90° for a few minutes and then poured into water, o-nitrobenzoylactic acid, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CO_2H$, separates, and may be purified by crystallisation from water. It melts at about 118°, and when boiled with water is decomposed into o-nitroacetophenone and carbon dioxide.

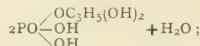
(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

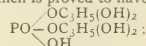
NOTE.—All degrees of temperature are *centigrade* unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxviii., No. 1, January 4, 1904.

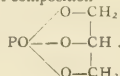
Phosphoric Ethers of Glycerin.—P. Carré.—In a preceding paper the author shows that the etherification of phosphoric acid by glycerin gives rise to three ethers. He now investigates—(1) The glycerophosphoric acid, which on heating is partially decomposed into phosphoric acid and a diether,—



(2) the diether, which is proved to have the composition—



and (3) the triether, of composition—



Retrogradation and Coagulation of Amidon.—L. Maquenne, A. Fernbach, and J. Wolff.—The authors find that starch coagulated by amyl-coagulase is like retrograde amidon, a complex mixture which is only partially saccharifiable—and that the diastatic coagulation of starch, judged from the nature of the resulting products, can be compared to the phenomenon described by one of the authors under the name of retrogradation. It can be distinguished by the rapidity with which the change takes place, the effect being to arrive almost instantaneously at the same result as would be observed when starch is left for a long time to itself.

Sodium Monosulphide as an Indicator in the Estimation of Glucose by Fehling Solution.—L. Beulaygue.—In order to assist in the measurement of the point of complete decolouration of Fehling's solution, and, consequently, the end of the reaction, the author finds certain indicating reagents of great value. For this purpose, monosulphide of sodium is used, dissolved in ten times its weight of distilled water. A drop of this substance on a piece of filter-paper acts as an indicator with the reduced Fehling solution, for when the liquid is not fully reduced a black or brown stain of copper sulphide is produced. This disappears directly reduction is complete, the filter-paper stain remaining colourless. The end of the reaction can in this manner be very sharply defined.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. W. B. Byran, Mr. C. E. Challis, Mr. A. F. H. Dick, Mr. W. B. Gowland, Sir Charles Hartley, K.C.M.G., Miss C. Jones, Mr. C. E. Layton, Mr. C. F. Lan-Davis, Mr. H. Loeffler, Brigade Surgeon Lieut.-Col. C. W. MacRury, Mr. W. M. Ogilvie, Mr. C. G. P. Pownall, Lady Priestley, Mr. C. F. Rousselet, R. E. Tatham, and Mr. J. Weir were elected members. The special thanks of the Members were returned to Sir Andrew Noble, Bart., Dr. Frank McClean, Mr. J. B. Brönn-Morison, J.P., and Lord Greenock for their donations to the Fund for the Promotion of Experimental Research at Low Temperatures.

Chemical, Metallurgical, and Mining Society of South Africa.—Annual Competition.—It has been decided to make six awards annually of £50 each, accompanied by a gold medal and diploma, for the following subjects:—(1) Mining; (2) Milling; (3) Cyaniding; (4) Chemistry, Pure and Applied; (5) Metallurgy (other than Milling and Cyaniding); (6) Agricultural Chemistry. The following are the conditions:—

- In awarding the prizes submitted for competition by members, associates, and students, all papers other than those by hon. members to be considered.
- The above awards to be made by specially constituted Committees, consisting of three members of the Society for each class, to be elected at a Special General Meeting of the Society, such Committees having power to refer selected papers to one or more competent authorities. The awards to go by a majority of votes and to be confirmed by the Council.
- No one to be awarded the prize in the same class two consecutive years.
- During the first year, ending June, 1904, no member of the Council may receive the cash prize, but may be awarded a Society's medal and diploma. In the event of any one of the Council being credited with the best contribution in any class, such member of Council would be awarded a Society's medal and diploma, whilst the cash prize, accompanied by a diploma, would fall to the ordinary member giving the next best paper in the same class.

- No one to be eligible for more than two prizes or two medals in the same year.
- In awarding the prizes, papers dealing with or having application to the South African Mining Industry to have preference. In the event of the prize awarding Committees considering that any paper submitted is not of sufficient interest to merit a prize, the prize may be withheld.
- No competitor to be allowed to adjudicate upon his own paper.
- In the event of circumstances arising such as are not provided for in the above conditions the Council shall have power to deal with the same.

A sixth prize of £50, accompanied by the Society's special gold medal and diploma, for the paper of the greatest utility to the Mining Industry, shall be open to the whole membership of the Society, and the adjudicating Committee shall consist of those members of the Council who do not compete, with power to take advice from expert authorities.

Yellow Arsenic.—MM. Erdmann and V. Unruh.—The authors have undertaken the examination of the yellow modification of arsenic already mentioned by other chemists. This yellow modification of arsenic, which corresponds to white phosphorus, is prepared by cooling arsenical fumes very rapidly. The sublimation is effected by heating arsenic in a tube of aluminium at the ordinary pressure. The fumes are carried in a current of an inert gas, such as carbonic acid. The arsenic must be heated to above 360°, and the fumes condensed very rapidly by very energetic cooling. By condensing the fumes at 360° we obtain metallic arsenic; by condensing at about 210° we obtain a black powder. As the yellow arsenic is further very rapidly transformed in the solid state into the black modification, we collect it in bisulphide of carbon, which dissolves the yellow variety. Finally, the whole of the apparatus must be protected from the action of light, which facilitates the transformation of the yellow arsenic into ordinary arsenic. See the original article for the apparatus used by the authors. The sulpho-carbonic solution, concentrated to saturation, and cooled in the dark in a mixture of CO₂ and ether at a temperature of at least -70°, leaves a deposit of arsenic in the form of a yellow powder. This yellow arsenic will keep without change in the dark at a temperature of -65° to -70°. Its solubility in bisulphide of carbon for 100 c.c. of the solvent is:—

Temperature.	Arsenic.
+46	11.0
+18—20	7.5—8.0
+12	5.5—6.0
+0	3.8—4.0
-15°	2.0—2.5
-60	0.8—1.0
-80—85	insoluble

It is slightly soluble in benzene, and still less so in acetic ether. In these sulpho-carbonic solutions the authors have also observed the formation of a precipitate of a brownish red colour adhering as a rule to the sides of the vessel; this represents a third modification of arsenic. This modification is stable when exposed to light, and recalls the red modification of phosphorus. The brownish-red arsenic has not been obtained entirely free from sulphur; it is very probably identical with the brown arsenic observed by Geuther (*Genaisch Zeit. f. Medizin. u. Naturw.* vol. x., suppl. p. 123), and obtained by him by the reduction of arsenious acid with trichloride of phosphorus. The molecular weight of the yellow arsenic, determined by Erdmann and Unruh's method (*Zeit. Anorg. Ch.*, vol. xxxii., p. 413), corresponds to As₄.—*Zeit. Anorg. Chem.*, vol. xxxii., p. 437.

Some Salts of Cadmium.—H. Grossmann.—This paper deals with the thiocyanates which have been also examined by MM. Meitzendorf (*Pogg. Ann.*, vol. lvi., p. 81) and Walden (*Zeit. Anal. Chem.*, vol. xxxii., p. 373).

To obtain the simple salt $(\text{CyS})_2\text{Cd}$, it is best to react with equal molecules of SO_4Cd and $(\text{CyS})_2\text{Ba}$ (obtained from CySNH_4 and $\text{Ba}(\text{OH})_2$; filter, and on evaporation we obtain crystalline crusts. If we boil a solution of CySNH_4 with $\text{Cd}(\text{OH})_2$ recently precipitated and freshly washed, NH_3 is given off, and the oxide is dissolved; after prolonged boiling, filtration, and evaporation on the water-bath, we obtain a liquid which, in the desiccator, gives fairly large but easily decomposed crystals of the mono-ammoniacal salt, $(\text{CyS})_2\text{Cd} \cdot \text{NH}_3$, in clinorhombic prisms, $m \text{ h}^1 \text{ g}^1$; $m \text{ m} = 104^\circ$; $m \text{ p} = 107^\circ 45'$; cleavages, $\text{h}^1 \text{ g}^1$. An excess of ammonia converts this salt into a diammoniacal salt, $(\text{CyS})_2 \cdot 2\text{NH}_3$, described by Meitzendorf. In these preparations there is also formed a double salt which is found in the mother-liquors, $(\text{CyS})_2\text{Cd} \cdot 2\text{CySNH}_4 + 2\text{H}_2\text{O}$; it is deliquescent, fuses at 25° , and is insoluble in alcohol. It forms clinorhombic prisms, θ dominant, $m \text{ h}^1 \text{ a}^1$, $m \text{ p} = 77^\circ 22'$, $\text{p h}^1 = 98^\circ 56'$. Other double salts, soluble and well crystallised, have also been prepared. Cadmico-potassic thiocyanate, $(\text{CyS})_2\text{Cd} \cdot 2\text{CySK} + 2\text{H}_2\text{O}$, in regular octahedra. Thiocyanate of rubidium, CySRb , in long needles similar to CySK , from CO_3Rb and CySNH_4 . Thiocyanate of cadmium and rubidium, $(\text{CyS})_2\text{Cd} \cdot 2\text{CySRb} + 2\text{H}_2\text{O}$, in hexagonal plates. The double salt of sodium is $(\text{CyS})_2\text{Cd} \cdot \text{CySNa} + 3\text{H}_2\text{O}$, in regular hexagonal plates, p m h^1 . For the double salt of barium, the slightly soluble simple salt of cadmium is first formed; the concentrated mother-liquors eventually give large deliquescent plates of $(\text{CyS})_2\text{Cd} \cdot 4(\text{CyS})_2\text{Ba} + 10\text{H}_2\text{O}$.—*Berichte*, vol. xxxvi., p. 2665.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Ash in the Human Body.—Will any reader kindly quote the proportion of ash in the human body, giving authority?—X.

MEETINGS FOR THE WEEK.

- MONDAY, 8th.—Society of Arts, 8. (Cantor Lectures). "Oils and Fats—their Uses and Applications," by J. L. Lewkowitch, Ph.D., &c.
- TUESDAY, 9th.—Royal Institution, 5. "Development of Animals," Society of Arts, 4.30. "The Biology of Federation," by the Hon. Sir John Alexander Cockburn, K.C.M.G.
- WEDNESDAY, 10th.—Society of Arts, 8. "Thermit—its Application to Metallurgical Engineering," by Charles Vernon Boys, F.R.S.
- THURSDAY, 11th.—Royal Institution, 5. "Recent Research in Agriculture," by A. D. Hall, M.A.
Society of Arts, 4.30. "Our Commercial Relations with Afghanistan," by Colonel Sir Thomas H. Holdich, R.E., K.C.M.G., K.C.I.E., C.B.
- FRIDAY, 12th.—Royal Institution, 9. "Westminster Abbey in the Early Part of the Seventeenth Century," by The Very Rev. J. A. Robinson, D.D.
Physical, 8. (At the Royal College of Science, South Kensington). Annual General Meeting. Address by Dr. R. T. Glazebrook, F.R.S., President.
- SATURDAY, 13th.—Royal Institution, 3. "Culture and Sculpture," by Charles Waldstein, Litt.D.

INSTRUCTION IN

PURE CULTIVATION OF YEAST. According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts brewers', distillers', wine, disease yeasts), moulds, and bacteria.

Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jørgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufactories, &c.

Further particulars on application to the Director—

ALFRED JØRGENSEN, The Laboratory, Copenhagen, V.

MACMILLAN'S BOOKS ON CHEMISTRY.

Fractional Distillation.

By SYDNEY YOUNG, D.Sc., F.R.S., Professor of Chemistry in University College, Bristol. With 72 illustrations.
Crown 8vo, 8s. 6d.

CHEMICAL TRADE JOURNAL.—Supplies a long-felt want. . . The whole of the chapters are easy and pleasant reading, and tempt the reader onward to the conclusion. . . We feel sure that every chemist who is interested in, or engaged with, any manufacturing process in which distillation is practised, will feel genuine pleasure in perusing this work, in studying the points of the various chapters, and in repeating some of the many experiments so fully described by the author.

SECOND EDITION, REVISED AND ENLARGED.

A SYSTEMATIC SURVEY OF THE ORGANIC COLOURING MATTERS.

Founded on the German of Drs. G. SCHULTZ and P. JULIUS. Revised throughout and greatly enlarged by ARTHUR G. GREEN, F.I.C., F.C.S., Professor of Tinctorial Chemistry at the Yorkshire College, Leeds; late Examiner in Coal-tar Products to the City and Guilds of London Institute.

Imperial 8vo, 21s. net.

THE CHEMISTRY OF PLANT AND ANIMAL LIFE.

By HARRY SNYDER, B.S.,

Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Agricultural Experiment Station.

Globe 8vo, 6s. net.

ELEMENTS OF INORGANIC CHEMISTRY.

By HARRY C. JONES,

Associate Professor of Physical Chemistry in the Johns Hopkins University.

Crown 8vo, 6s. 6d.

THEORETICAL ORGANIC CHEMISTRY.

By JULIUS B. COHEN, Ph.D., Lecturer on Organic Chemistry, The Yorkshire College; Lecturer in the Victoria University.

Globe 8vo, 6s.

NATURE.—"The book is well printed, and the proofs have evidently been very carefully corrected. Taken as a whole, we consider Dr. Cohen's book a very useful compilation."

A COLLEGE TEXT-BOOK OF CHEMISTRY.

By IRA REMSEN, President of Johns Hopkins University.

Extra Crown 8vo, 8s. 6d. net.

GUARDIAN.—"The author's skill in writing elementary text-books is well known, and this work displays the features by which his other writings of the kind are characterised."

THIRD EDITION NOW READY.

INTRODUCTION TO PHYSICAL CHEMISTRY.

By JAMES WALKER, D.Sc., Ph.D., F.R.S.,

Professor of Chemistry in University College, Dundee.

Third Edition. 8vo, 10s. net.

THE PRINCIPLES OF INORGANIC CHEMISTRY.

By WILHELM OSTWALD.

Translated with the Author's sanction by ALEXANDER FINDLAY, M.A., B.Sc., Ph.D. With 122 Figures in the Text.

8vo, 18s. net.

NATURE.—"Prof. Ostwald's style is excellent, and full justice is done to it by Dr. Findlay's translation; hence the book is most readable and interesting. . . It is unnecessary to mention that the work is entirely up to date."

PRACTICAL CHEMISTRY.

An Experimental Introduction to Laboratory Practice and Qualitative Analysis from a Physicochemical Standpoint.

By R. ABEGG and Professor W. HERZ.

Translated with the Authors' sanction by H. T. CALVERT, B.Sc. (Vict.), A.I.C. With Three Tables.

Crown 8vo, 6s.

MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2307.

ON THE COLORIMETRIC DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID AND OF SILICA.*

By F. P. VEITCH.

In some of the field work of this bureau the analysis of drainage waters and of water extracts of soil is required daily. For this purpose the usual gravimetric processes are deemed impracticable on account of the time required, and it has been necessary to use more rapid volumetric, colorimetric, and photometric methods.

The writer suggested, and in the spring and early summer of the past year made an examination of, some known rapid colorimetric methods for the determination of phosphoric acid and of silica in these soil solutions. Incidentally, as the presence of iron in considerable amounts introduces errors in the determination of phosphoric acid, the rapid methods for the detection and estimation of minute quantities of iron have received some attention. As these latter methods have been thoroughly worked out and are quite well known, but passing reference need be made to them here.

For the estimation of phosphoric acid, the method described by Lepiere (*Bull. Soc. Chim.*, 1896, xv., 1213) and later studied in more detail by Woodman and Cayvan (*Journ. Am. Chem. Soc.*, xxiii., 96) promised to be the most rapid and to present the fewest difficulties in its manipulation.

For the adaptation of this method to the analysis of soil solutions, the influence of other compounds, both organic and inorganic, must be eliminated or determined. It was found that turbidity, organic matter where it produced a coloured solution, ammonia salts in large amounts, iron salts in small amounts, dissolved silica, and filter-paper introduce errors which are not negligible.

Removal of Suspended Matter.

Turbidity may be removed by filtering through a Chamberland filter, which of course removes some of the phosphoric acid from the first runnings (see Table VIII.). It may also be quite largely, sometimes completely, removed by evaporation to dryness and filtering; or it may be corrected for by matching the standard phosphomolybdate solution against the turbid solution and subtracting this reading from the final readings. None of these procedures is perfectly satisfactory, but nothing better has yet been devised. All have been used here, according to the difficulties presented. Where filtration will remove all suspended matter, this procedure is to be preferred, but as this cannot always be accomplished, the Chamberland filter or evaporation must be resorted to.

In the work about to be described the reagents were prepared as directed by Woodman and Cayvan (*loc. cit.*) and were free from interfering substances. The same lot was used throughout the work, and all work was done at from 18°—22° C., the standard and the unknown solution being of course at sensibly the same temperature.

Removing Organic Matter.

Organic matter which colours the solution at all must be removed, or it must be corrected for as above described, before reliable readings can be made. To accomplish this, two methods were tried: treatment with aqua regia, and ignition with magnesium nitrate. Several treatments with

aqua regia were required to insure the destruction of all organic matter, after which the solutions were carried to dryness, taken up with water and 2 c.c. nitric acid and compared in a reflecting colorimeter. The following readings were obtained:—

TABLE I.

	Amount P ₂ O ₅ added.	Amount P ₂ O ₅ recovered.
	Parts per Million.	
1	1.0	1.0
2	2.0	1.1
3	3.5	2.4
4	5.0	4.3
5	7.0	6.1
6	9.0	7.1

We see that there is considerable loss of phosphoric acid from this concentrated aqua regia solution, a fact previously pointed out by Woodman and Cayvan.

Other phosphate solutions were then treated with magnesium nitrate free from silica, evaporated to dryness with nitric acid, and ignited in a porcelain dish until all carbon was burned off. The residue was then taken up with water and nitric acid, and compared with the standard solution.

TABLE II.

	Amount P ₂ O ₅ added.	Amount P ₂ O ₅ recovered.
	Parts per Million.	
1	1.0	1.0
2	2.0	1.8
3	4.0	3.7
4	6.0	5.9
5	8.0	7.9
6	9.0	9.2
7	10.0	9.9
8	3.0	2.7
9	1.0	1.0
10	5.0	5.2
11	10.0	10.6

Average loss .. 0.06

The loss here is quite small, being as a rule within the limit of error of the reading. From these experiments it appears that the organic matter may be satisfactorily removed without loss of sensible amounts of phosphoric acid by ignition with magnesium nitrate and subsequent evaporation with nitric acid.* It may be said, however, that when the colour due to organic matter is not greater than 0.2 to 0.3 part per million, it is hardly worth while to remove the organic matter, as a correction may be made for it by reading the colour due to organic matter against the standard, and correcting the final reading by the reading thus obtained.

The volatility of phosphoric acid upon evaporation of these water solutions is at first sight rather startling to analysts, and while there is not the slightest doubt that it does take place from solutions of phosphoric acid and from disodium phosphate solutions, there appears to be no reason to think that it occurs from solutions containing sufficient bases to form the normal phosphates. In no case has the writer obtained a loss from solutions of this character. As phosphates dissociate readily, it seems possible that water extracts of soils may contain occasionally some free phosphoric acid or acid phosphates from which phosphoric acid is partly volatilised upon evaporation. That this does not take place in the presence of a large excess of base, even from acid solutions, is shown positively by the experiments with magnesium nitrate.

Influence of the Presence of Other Salts.

Ammonia salts in considerable quantities decrease slightly the intensity of the colour reaction. Ammonium

* Subsequent work has confirmed these results in every instance.

† It seems possible that this apparent loss may be due to the formation of pyrophosphoric acid. — *Eng. Am. Chem. Soc.*

* From the *Journal of the American Chemical Society*, xxv., No. 2.

nitrate added to the unknown solution at the rate of 0.04 grm. per 50 c.c. gave readings on 4 parts per million of standard of only 3 parts, which increased a little on standing, but the solution soon precipitated. Ammonium chloride does not give a water-white solution always—has a tendency to be slightly opaque, and it also prevents the full development of the colour. The figures obtained are given in the table.

TABLE III.—Effect of Ammonium Salts.

Parts per million NH_4NO_3	Parts per million P_2O_5 added to NH_4NO_3 solution.	Parts per million P_2O_5 without NH_4NO_3 .	Solution with NH_4NO_3 commenced to precipitate.
4000	1.0	0.7	Not in five minutes.
4000	4.0	2.0	Nearly as dark, but precipitated too rapidly to be sure.
4000	3.0	3.0	Precipitated in fifty minutes.
800	4.0	3.3	Precipitated in seventy minutes.
800	4.0	3.7	

Calcium nitrate, barium chloride, potassium nitrate, and aluminum sulphate, separately and together, were added to solutions at the rate of 0.25 grm. of each salt to 50 c.c. of solution. None of these except the aluminum sulphate affected the readings more than 0.1 part per million, or within the limit of error of readings. Aluminum sulphate in this quantity gave a dark, opaque solution which could not be matched satisfactorily against the standard.

It was found that iron salts in considerable quantities exerted a marked influence not only on the colour of the

solution itself, in the first instance, an influence which it was found could be corrected for by reading against the standard, but there is also a reaction between the iron salt and the molybdate, a reaction which appears to bear a relation to the amount of iron present, and which possibly may be used for the estimation of the iron in solution. As iron is present in many soil extracts, the reaction of iron with the molybdate solution required careful study in order to determine the amounts and conditions which would vitiate the phosphate readings. The results of the investigation of this point are given in Table IV. Unless otherwise stated, the two solutions were identical in all particulars except that one contained iron in the amounts given in the table. The iron salt was made from pure wire, the solution of which was evaporated to dryness several times to remove traces of silica and hydrochloric acid.

The presence of less than 20 parts of iron (Fe) per million of solution introduces no appreciable error in the determination, while as much as 50 parts per million vitiate the phosphate results, unless the amount of iron present is known and its reading subtracted from the total reading. As soil extracts seldom contain more than 0.1 to 5 parts per million of iron, further study of the influence of iron has been temporarily discontinued, but it is hoped to devote more attention to this point later. It is of course necessary, where the presence of considerable iron is indicated, to assure one's self that not more than 20 parts per million are present before the reading can be accepted as representing phosphoric acid alone. This is quite readily ascertained by adding potassium sulphocyanide or ferrocyanide to the acidulated extract, and matching the developed colour against an iron standard (Sutton's "Volumetric Analysis," eighth edition, p. 245).

(To be continued).

TABLE IV.—Colour produced by Iron Salts with Molybdate Solution.

Parts per million of Fe in solution.	Parts per million of P_2O_5 to equal colour of Fe solution—		Parts per million of P_2O_5 to equal colour produced by adding 1 part per million P_2O_5 to Fe solution containing molybdate.
	Before molybdate was added.	After molybdate was added to Fe solution.	
<i>Preliminary Series.</i>			
4000	3.0	6.5	—
2000	—	3.0	—
2000	0.6	2.5	—
2000	—	4.0	1.05
2000	—	3.1	0.95
2000	—	3.0	1.10
400	2.2	3.2	—
200	0.8	1.6	1.10
80	0.2	0.8	1.00
40	0.1	0.3	1.00
40	0.1	0.5	—
40	0.1	0.5	1.00
<i>Final Series.</i>			
100	0.1	0.75	{
		0.75	
		0.80	
50	0.0	0.40	{
		0.40	
		0.50	
20	0.0	0.10	{
		0.10	
10	0.0	0.00	{
		0.00	
8	0.0	0.00	{
		0.00	
4	0.0	0.00	{
		0.00	
		0.00	
	0.0	0.00	{
		0.00	

ON THE PART PLAYED BY BENZENE IN POISONING BY COAL-GAS.*

By R. STAEBELIN, M.D.,
Senior Assistant in the Medical Clinic at Basel.

IN a recent paper Vahlent† has maintained that a difference exists between the poisonous action of coal-gas and of carbon monoxide, and Kunkel‡ has also drawn attention to a similar difference in the case of frogs. In the course of a research which I was undertaking in University College for other purposes, at the suggestion of Prof. Starling, I have come across facts which may serve to explain the difference noted by these observers.

My first object was to investigate the effect of deprivation of oxygen on the fatigue curve of muscles. To this end, a muscle was hung up in a closed chamber, and the atmospheric air driven out by a stream of some other gas. When coal-gas was used for this purpose, it was noticed that the muscle rapidly went into *rigor mortis*, whereas, in nitrogen, it remained excitable for many hours. I set myself, therefore, to find out which constituent of the coal-gas was responsible for this poisonous effect.

The experiments were carried out on the frog's sartorius, since the relatively large surface of this muscle renders it particularly accessible to gaseous poisons. The muscle was hung up in a glass tube, closed above and below by rubber corks. To the upper cork a hook was fastened on which was hung the bony insertion of the sartorius. Through the lower cork a glass tube passed. The movements of the muscle were transmitted to a recording lever

* A Paper read before the Royal Society, January 28, 1904.

† Ferchlend and Vahlen, "Ueber Verschiedenheit von Leuchtgas- und Kohlenoxydvergiftung," *Archiv für Experimentelle Pathologie und Pharmacologie* xlviii., p. 106; Vahlen, "Ueber Leuchtgasvergiftung," *Ibid.*, xlix., p. 245.

‡ Kunkel, "Ueber Verschiedenheit von Leuchtgas- und Kohlenoxydvergiftung," *Sitzungsberichte der Physikalisch-medizinischen Gesellschaft zu Würzburg*, 1902, No. 4, v., p. 61.

by means of a steel needle hooked into the lower end of the muscle and passing through the glass tube. The lever was weighted near its axle, and was after-loaded, and its movements were recorded on a slowly rotating drum, on which the time was also marked by means of a signal. The closed tube was provided with two small lateral openings by which any gas desired could be passed through it, the opening through which the needle passed to the lever being made sufficiently air-tight by means of a small plug of vaseline. In every experiment two similar apparatus were employed, so that the influence of two gases could be compared at one and the same time on the two sartorii of the same frog.

When coal-gas was led through the tube the muscle began to contract one to seven minutes after the beginning of the passage of the gas, and in half to one hour the muscle was maximally contracted, and had an opaque appearance. The rapidity with which the contraction came on was proportional to the rapidity with which the gas was passed through the chamber and varied with the temperature, warmth quickening and cold slowing the process. Once the muscle was fully contracted no recovery took place. This phenomenon could not be due to the CO in the coal-gas, since, on passing pure CO through the muscle chamber, the muscle remained excitable as long as in nitrogen, and the fatigue curve took the same course as in that gas. Among the remaining more important constituents of coal-gas which might produce this phenomenon, benzene merited first attention, since all aromatic bodies are more or less potent poisons. I therefore tried the effect of passing air through benzene into the muscle chamber. I found that in less than a minute the muscle began to contract, and the contraction reached its maximum height within a short time, the muscle becoming opaque and dead. The other sartorius of the same frog was placed at the same time in coal-gas. It began to contract only after several minutes, and the contraction took half-an-hour to reach its maximum. Benzene vapour therefore showed itself much more poisonous for a muscle than coal-gas, evidently on account of its greater concentration. According to Letheby, London coal-gas contains only 3.8 per cent of condensable hydrocarbons of which benzene forms only a small proportion. I therefore, in another experiment, passed air into the muscle chamber, not through pure benzene, but through water which had been shaken up with benzene. In this case the contraction began six minutes after the beginning of the experiment, and took thirty-eight minutes to reach its maximum, while the control muscle in coal-gas began to contract in seven minutes, and reached its maximum contraction in forty minutes.

It seemed, therefore, highly probable that benzene was really the constituent of coal-gas which was responsible for its toxic properties on muscle. If that were the case the passage of coal-gas through oil, which absorbs benzene, ought to deprive it of its deleterious effects. This was found to be the case. Coal-gas, passed through oil, showed no difference in its effects from pure CO or nitrogen.

In the same manner as benzene I investigated the effects of xylol and toluol. If the muscle was supplied with air blown through either of these fluids no poisonous effect was observed even when the fluids were warmed. The absence of effect in these two cases is perhaps to be ascribed to the lower vapour tension of these two substances. The muscle was equally unaffected when supplied with air which had been passed over heated naphthalene.

I also investigated the effect of certain hydrocarbons of the fatty series, namely, methane, prepared by heating sodium acetate and sodium hydrate, acetylene produced by the action of water on calcium carbide, as well as the mixture of substances obtained by blowing air through petroleum ether. In none of these cases was any effect produced on the muscle. If, however, a trace of benzene was added to petroleum ether, *rigor mortis* of the muscle was almost immediately produced. In this case the volatility of the petroleum ether apparently aids the evolu-

tion of the benzene. On the other hand, the addition of small quantities of benzene to xylol does not impart poisonous qualities to the air bubbled through the mixture, the benzene being apparently held fast by the less volatile xylol.

It seemed, therefore, most probable that the specific poisonous effect of coal-gas on frog's muscle was due to benzene only, and that it was to the presence of this substance in coal-gas that the differences observed by Kunkel and Vahlen between the action of coal-gas and carbon monoxide were to be referred. Vahlen states that warm-blooded animals and frogs die more rapidly in coal-gas than would be expected from its percentage of CO, and also that frogs in coal-gas present excitatory phenomena which are absent in pure CO. Although Kunkel denies the presence of any difference between the action of these two gases on warm-blooded animals, he also draws attention to the peculiar effects on frogs of coal-gas, which are not produced by other gases free from oxygen, and describes them as "choreform twitches and spasms in the neck and legs." To decide this question the following experiments were carried out:—

I. Three frogs were placed in air-tight bell jars, through each of which coal-gas was conducted at constant rate. The coal-gas had to pass in each case through a wash bottle, which in A was water, which, of course, left the composition of the gas unchanged, in B oil, which would absorb the benzene. In front of C were two wash bottles, the first one containing oil, the second one benzene.

The passage of the gas through the three bell jars was begun at 11.20. At 11.25 all three frogs were restless. Frog C remained then still for a short time, and the breathing became irregular, and twitching occurred in the extremities and back. Movements were chiefly co-ordinated, though there were some twitches of isolated muscles. After a little time the movements became shorter and less co-ordinated, the legs remained stretched out, and breathing ceased. Frog A betrayed phenomena similar to C, but the spasms were less evident, and came on more slowly. Frog B became quite quiet, the respiration becoming irregular and shallower.

At 11.40 B was sitting up in normal position, though the breathing was somewhat irregular, while A and C were lying on their bellies, with legs stretched out. At 11.45 all three frogs were taken out. C gave no signs of life, and in ten minutes was quite rigid; B still reacted slightly to stimulation, showed shallow respiratory movements, and gradually recovered, so that at 1.30 it was apparently normal. Frog A at first showed no response to stimulus, and no respiratory movements. By 11.55 it had recovered sufficiently to show both these phenomena, and at 1.30 it was so far recovered that it could recover its position when turned on its back, and in a couple of hours later was apparently normal.

II. In a second experiment the arrangements were the same as in the first, except that in C the gas which had passed through the oil was allowed to pass through water saturated with benzene instead of through pure benzene. In this case the phenomena in A and C were practically identical, and were similar to those observed in A in the first experiment. We need not, therefore, give fuller details of this experiment.

We thus see that, when frogs are exposed to coal-gas, motor phenomena are produced, which are absent if the coal-gas be previously purified by passage through oil, and that these phenomena can be reproduced if the purified gas be made to take up benzene vapour. The poisonous properties of the gas can be increased by increasing the tension of the benzene vapour. We are therefore justified in concluding that the differences between the effects of CO and coal-gas, observed by Kunkel and Vahlen, depend on the presence in the latter of benzene. The slight motor excitation observed in frogs in coal-gas, which had been purified by passage through oil, is exactly similar

to that described by Kunkel, as the result of deprivation of oxygen, produced by placing the frogs in nitrogen or CO, as is shown by the following experiment :—

III. Two frogs were placed, one in a bell jar through which CO gas was led, the other in a similar jar through which coal-gas was led after passing through oil. Both animals in a short time showed slight twitchings of isolated groups of muscles in the extremities and back, and occasional extensor movements of the hind limbs which gradually diminished. No difference was observable between the two frogs. In three-quarters of an hour they were taken out of the jars, and both recovered within a short time.

In order to be certain of the part played by benzene in coal-gas poisoning, we must have some idea of the effect of pure benzene on the frogs. I have been unable to find any published experiments over the effects of inhalation of benzene on the frog. Beyer* states that xylol acts as a narcotic poison, like the other odorous substances investigated by him. I have therefore made some experiments on the influence of benzene vapour in the presence of oxygen on frogs.

IV. A frog was placed in a bell jar, in which a beaker of benzene was hung up. Eight minutes after the beginning of the experiment spasmodic movements and twitchings began in various parts of the body, accompanied by a considerable secretion of mucus. After a few minutes the spasms ceased, the frog lay still with extended limbs, and respiration, which at first was irregular, became gradually shallower and less frequent. Twenty minutes after the beginning of the experiment all respiratory and other movements had ceased. The frog was taken out of the jar, and recovered in a few hours.

In other experiments in which the frog was left longer exposed to the action of benzene vapour, *rigor mortis* came on first in the hinder and then in the fore extremities before the heart had ceased to beat. One peculiarity was observed with regard to the reflex irritability of the animals, under these conditions, which is worthy of notice. Very early in the experiment, at the very beginning of the spasmodic movements, the frog reacted very slightly and incompletely to changes in its position, that is, such as would be produced by holding the vessel in which they were placed in an oblique position or turning them on their sides or backs. On the other hand, the reactions to tactile stimuli of the skin were much more pronounced than usual, so that a tap on the one foot might evoke muscular contractions throughout the whole body. When the animals began to become rigid, stimulation of a toe of the rigid limb could evoke contractions of the limbs which had not yet become stiff. Thus, in all these experiments the first result of the poisoning was motor excitation, which showed itself at first by co-ordinated movements affecting large portions of the body, and later by twitchings of isolated groups of muscles. A little later the respiration became irregular, and finally ceased. The higher reflexes, e.g., the reaction to changes in position, were abolished, while the lower were increased. Finally, however, the paralysis became universal, so that also the spinal reflexes were abolished. This stage was followed by a rigidity of the muscles, and last of all the heart ceased to beat. The rapidity of onset of these phenomena is naturally dependent on temperature, being quicker the higher the external temperature. It is evident that we have, therefore, to deal with an action of the poison on the central nervous system. The general spasmodic movements are abolished by previous destruction of the brain and spinal cord; the twitchings of the muscles and the rigor of the extremities persist, however, in the complete absence of the central nervous system, and occur in a hind limb, the nerve of which has been divided, as rapidly as on the opposite side.

The onset is not prevented by curiarisation, and must therefore be ascribed to a direct action of the benzene on the muscles themselves, as has been described at the beginning of this paper.

In the poisoning by coal-gas this rigor of the muscles was not observed either by myself or Vahlen and Kunkel, probably because the animals die of asphyxia before the small amounts of benzene present in the coal-gas have time to bring about their direct effect upon the muscular tissue. As Experiment I. shows, the increase in the percentage of benzene in the coal-gas is followed by the onset of rigidity in the muscles.

Rather more difficult is the explanation of the increased reflex excitability in the later stages of intoxication. It may be that the poisonous effects are first confined to the higher centres. On the other hand, the increased irritability of the muscles themselves is the chief factor in the spinal reflex hyper-excitability. In coal-gas poison, when the lower centres are also paralysed by asphyxia, the reflex excitability disappears.

It is thus possible to refer the difference between intoxication by coal-gas and that by CO entirely to the influence of benzene, which determines in its first stage vigorous excitatory motor phenomena. In warm-blooded animals the conditions are quite different. Lorraine Smith* found that an addition of 0.65 percent of benzene to air had no effects on a guinea-pig, and Santesson† did not succeed in producing either acute or chronic poisonous effects by administering benzene to a rabbit by inhalation. In man, too, cases of poisoning by benzene are few and far between. It is possible that the minute quantities which are absorbed by the lungs are rapidly oxidised and excreted as an aromatic sulphate. At any rate, in man, benzene plays no part in the poisonous effects of coal-gas.

Summary of Results.

1. Coal-gas produces first excitation and then rigor of the isolated frog's muscle.
2. Frogs exposed to coal-gas show excitatory phenomena which are absent when the animal is placed in an atmosphere of CO or nitrogen.
3. The specific effects of coal-gas on frogs are determined by the presence of benzene in the gas, and can be produced by air containing the same percentage of benzene.
4. There is no reason to suppose that the poisonous effect of coal-gas on mammals is determined by anything except its content in CO.

PRECIPITATION AND SEPARATION BY WEAK ORGANIC BASES.‡

By E. T. ALLEN.

(Continued from p. 65).

Separation of Titanium from Beryllium.

It has been shown that the elements of the quadrivalent family, Ti—Th, are, with the exception of Ce, separable from iron by phenylhydrazine. Beryllium forms a much weaker base than ferrous iron, but it may be separated from titanium and zirconium in a fairly satisfactory manner by similar means. The tendency is for the beryllium also to be partly precipitated, and with sulphate solutions, especially where the quantities of the elements to be separated are considerable, satisfactory results are not obtained by two precipitations. The standard solution of beryllium employed in the work was the chloride. The source of it

* Beyer, "Narkotische Wirkungen von Riechstoffen und ihr Einfluss auf die Motorischen Nerven des Frosches," *Archiv fur Anatomie und Physiologie, Ph. siologische Abteilung*, 1902, p. 201.

* Lorraine Smith, "The Poisonous Action of Coal-gas and Carburetted Water-gas," "Report of the Water-gas Committee," presented to both Houses of Parliament by command of Her Majesty, 1899, Appendix VII., p. 127.

† Santesson, "Ueber Chronische Vergiftungen mit Steinkohlenbenzin," *Archiv fur Hygiene*, xxxi., p. 336.
From the *Journal of the American Chemical Society*, xxv., No. 4.

TABLE D.—Separation of Titanium from Beryllium (Double Precipitation).

No.	BeCl ₂ taken		BeO.	BeO found.	Error.	TiSO ₄ taken	TiO ₃ .	TiO ₃ found.	Error.
	C.c.		Grm.	Grm.	Grm.	C.c.	Grm.	Grm.	Grm.
1.	10	=	0'0101	—	—	10	=	0'0096	0'0000
2.	10	=	0'0101	—	—	10	=	0'0096	0'0000
3.	5	=	0'0050	—	—	25	=	0'0239	-0'0008
4.	30	=	0'0302	—	—	5	=	0'0048	+0'0021
5.	100	=	0'1006	0'0960	-0'0046	100	=	0'0958	+0'0038
6.	95	=	0'0956	0'0951	-0'0005	5	=	0'0048	+0'0006
7.	5	=	0'0050	0'0049	-0'0001	95	=	0'0910	+0'0001

TABLE E.

No.	BeCl ₂ taken		BeO.	BeO found.	Error.	Zr(SO ₄) ₂ taken.	ZrO ₃ .	ZrO ₃ found.	Error.
	C.c.		Grm.	Grm.	Grm.	C.c.	Grm.	Grm.	Grm.
1.	5	=	0'0050	—	—	95	=	0'0925	+0'0036
2.	95	=	0'0956	—	—	5	=	0'0049	+0'0012
3.	5	=	0'0066	0'0040	-0'0026	15	=	0'0438	+0'0020
4.	45	=	0'0591	0'0590	-0'0001	5	=	0'0049	+0'0003
5.	15	=	0'0196	0'0187	-0'0009	45	=	0'0438	+0'0005
6.	35	=	0'0458	0'0445	-0'0013	35	=	0'0341	+0'0018
7.	100	=	0'1305	0'1290	-0'0015	50	=	0'0506	+0'0014

was beryl from Chester County, Pennsylvania. I transformed this into the double fluoride by the method which Marignac used in extracting zirconia from zircon, viz., by fusing the powdered mineral with two or three times its weight of potassium fluoride. For convenience in handling, the fused mass may be poured out in a thin sheet into a platinum basin and subsequently powdered. It is then boiled several times with successive portions of water, to which should be added at first some hydrofluoric acid. The double fluorides which silicon and aluminum form with potassium are nearly insoluble in water containing potassium fluoride, and are thus for the most part left behind. The solution is now evaporated to a small volume and allowed to crystallise. The salt is then re-crystallised several times. It dissolves rather slowly in boiling water. Each time the last portion should be rejected. The compound still retains iron, which may be entirely removed by passing hydrogen sulphide through the aqueous solution, which is, of course, alkaline. The crystals may finally be dried at 105° C. It is a difficult matter to be sure of the complete absence of alumina, but the following determination indicates that the compound thus prepared is essentially pure. A weighed portion was changed into sulphate by heating with sulphuric acid, thence through the hydroxide to chloride, and finally to hydroxide again, which was ignited and weighed. To be sure that the beryllium oxide was free from sulphate, the precipitation with ammonia was, in fact, made three times. All the filtrates were evaporated to a small volume and treated with a little ammonia, which brought down a little beryllia, which was filtered and washed separately and added to the main portion. 1'2996 grms. gave 0'2008 grm. BeO; calculated for K₂BeF₆, 0'1993. I am not aware that this method has been used previously to extract beryllium from beryl. For the determinations which follow, a solution of beryllium chloride was prepared as above indicated. To separate titanium and zirconium from beryllium, it is not, of course, necessary to add any soluble sulphite. The acid solutions are merely brought nearly to neutrality with ammonia and then acidified with several drops of dilute hydrochloric acid. A double precipitation was made, and water only was used for washing. The solutions were heated but not boiled. As previously stated, the results were not so exact as in the separation of titanium and zirconium from ferrous iron.

The beryllium was determined in the filtrate from titanium by ammonia, as in an ordinary determination of aluminum. Subsequent experiments showed that phenylhydrazine precipitates a large fraction of the beryllium from a solution of the sulphate, but none from the chloride. It follows that a double precipitation by phenylhydrazine from a chloride solution would give a more exact separation from titanium than those recorded in Table D.

Separation of Titanium from Beryllium by Aniline.

No.	BeO taken.	TiO ₃ taken.	TiO ₃ found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0'050	0'1416	0'1422	-0'0006
2.	0'075	0'0944	0'0950	-0'0006

The solutions used were beryllium chloride and titanium sulphate. The mixtures were first changed to chlorides by precipitation with ammonia and subsequent solution in hydrochloric acid. From the chloride solution, a double precipitation was made by aniline.

Separation of Zirconium from Beryllium.

Everything that has been said as regards the separation of titanium from beryllium applies equally well here. (See Table E).

An inspection of the tables makes it plain that a little beryllium is sure to be carried down with the quadrivalent metal where sulphate solutions are used, but here too, as in the case of beryllium and titanium, we may confidently predict more accurate results if chloride solutions are taken.

Separation of Thorium from Beryllium.

No.	BeO taken.	ThO ₃ taken.	ThO ₃ found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0'025	0'2863	0'2847	-0'0016
2.	0'025	0'1909	0'1895	-0'0014

The solutions used were beryllium chloride and thorium nitrate. Separation 1 was made with phenylhydrazine, separation 2 with aniline. Double precipitations were made in both cases. Thorium is, of course, a stronger base than titania or zirconia. From the above solutions it did not precipitate until a boiling temperature was reached and the precipitate was very slimy, like alumina when precipitated under the same circumstances. This may account for the fact that the results are a little low.

Attempts to separate aluminum from beryllium, and chromium from beryllium, and from ferrous iron, all failed. Usually the bivalent metal was carried down in considerable quantities with the trivalent one. Chromium chloride does not easily precipitate with phenylhydrazine. Many experiments tried along the above lines show that two elements when too near the same basicity can not be separated by this method, though just why the bivalent element should be partly precipitated in the presence of the trivalent is not perfectly clear.

The Hydrolysis of Aniline and Phenylhydrazine Hydrochlorides.

The degree of hydrolysis which a salt suffers in aqueous solution may be estimated from its conductivity, the values observed being compared with those shown by salts

of the same type in which hydrolysis is negligible; or it may be calculated from the velocity of certain chemical actions which are caused by the free acid present in the salt solution. The best examples of the latter are the inversion of cane-sugar, and the saponification of methyl acetate. The last-named method was selected in this work (Walker, *Zeit. Phys. Chem.*, iv., 319). A medium temperature of 40°C . was chosen. It was maintained by thermostat of the Ostwald type, of 100 litres capacity, which could be held within limits of about 0.2°C . for long periods. All the experiments were made with N/10 solutions of the hydrochlorides of the two bases, phenylhydrazine and aniline. Several preparations were used that there might be reasonable certainty that the saponification constants were not affected in any considerable degree by impurities. Two different samples of "C.P." phenylhydrazine hydrochloride were purified by dissolving in alcohol and precipitating by ether. One specimen of aniline hydrochloride was prepared in a similar way, and another was made from pure aniline by evaporating with pure hydrochloric acid on the water-bath. All the preparations stood a long time in desiccators with lime and sulphuric acid, before use. The reaction vessels consisted of 8-inch test-tubes which were first treated for some time with steam, then boiled with concentrated hydrochloric acid, and finally very thoroughly washed and dried (Ley, *Zeit. Phys. Chem.*, xxx., 229; Walker, *Journ. Chem. Soc.*, lxx., 577). N/10 solutions of the hydrochlorides were employed in the saponification as representing on the average about the concentration of these salts in those solutions in which the separations were made. In detail, the proper quantities of the salts, viz., $0.324\text{ gm. C}_6\text{H}_5\text{NH}_2\text{Cl}$, and $0.361\text{ gm. C}_6\text{H}_5\text{N}_2\text{H}_2\text{Cl}$, were first weighed out and transferred to the reaction tubes. The latter were then constricted in the flame at a distance of 2 or 3 inches from the open end, after which 1 c.c. methyl acetate was introduced by a pipette about 2 m.m. in diameter, followed by 250 c.c. water free from carbonic acid. The tubes were then sealed, cooled, shaken to mix the contents, and placed in the bath. After a sufficient interval, a tube was withdrawn, chilled, and opened. Its contents were then tested as follows:—1 c.c. was removed by a pipette, added to a small volume of water free from carbonic acid, and titrated with N/20 soda, phenolphthalein serving as an indicator. The errors in measurement were reduced to a minimum by using narrow instruments. The pipette was about 2 m.m. in diameter and the 10 c.c. burette, about 8 m.m. During the titration, the contents of the burette were protected from the outer air by a soda-lime tube. The sodium hydroxide was prepared according to Ley (*Zeit. Phys. Chem.*, xxx., 205), and was proved free from carbon dioxide by titrating against N/10 hydrochloric acid, first with the aid of phenolphthalein, then with methyl orange.

1. Phenolphthalein used as indicator:—5 c.c. HCl = 9.58, 9.59, 9.58, 9.60 c.c. NaOH ; mean, 9.59 c.c.
2. Methyl orange used as an indicator:—5 c.c. HCl = 9.59, 9.52, 9.58, 9.59 c.c. NaOH ; mean, 9.57 c.c.

(To be continued).

Analysis of the Combustible Gas given off in the Caspian Sea, near the Gulf of Baku.—K. V. Charitchkof. —Taking the sample is a matter of some difficulty, and it is almost impossible to obtain the gas free from all admixture with atmospheric air; we have taken account, in the analysis, of this air, calculated on the quantity of oxygen measured. The gases, collected in two different places, are shown to be free from CO_2 , CO , and non-saturated hydrocarbons, neither do they contain hydrogen (tested for with palladium sponge by Hempel's method); they consist of methane and a little nitrogen:—

	First gas.	Second gas.
CH_4 , per cent	96.28	95.17
N, per cent	3.72	4.83

—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 712.

INSTITUTE OF CHEMISTRY.

At the January Examinations, 1904, the following questions were given:—

INTERMEDIATE EXAMINATION.

General and Theoretical Chemistry.

Tuesday, January 5th.

Not more than four of the following questions are to be attempted:—

1. How would you prepare silicon hydride, silicon fluoride, and an aqueous solution of silicic acid? What are the properties of these substances? What reasons exist for classifying silicon with carbon and tin.
2. Give an account of the oxides of lead, and explain the use of lead peroxide in the storage battery or accumulator.
3. How would you proceed to determine the composition of a sample of gas obtained by the action of a mixture of steam and air on red-hot coke?
4. Ethylene and ethylidene chlorides are isomeric substances. What is the evidence on which this statement is based, and how can the constitution of the chlorides be determined?
5. Describe fully the preparation in the pure state, the properties, and the reactions of any two of the following substances:—Allyl alcohol, lactic acid, acetophenone, resorcinol.
6. Explain the methods by which salicylic acid can be prepared synthetically. How may this acid be proved to be an ortho-derivative of benzene, and how may it be distinguished from its isomerides? How could it be converted into (a) benzene, (b) phenol, and (c) benzoic acid?

Not more than four of the following questions are to be attempted:—

7. Write an essay on nitrogen peroxide.
8. Describe the preparation in the pure state, appearance, and properties of two of the following substances:—Phosphonium iodide, hydroxylamine sulphate, sodium metabisulphite; potassium persulphate, anhydrous chromium chloride.
9. What is iron rust? What views are held with regard to the chemistry of the process of rusting? How do you account for the fact that tinned iron rusts more rapidly than galvanised iron when once the oxidation has begun?
10. What conclusions do you draw from the following results obtained in the course of the investigation of an ester:—(a) Found, $\text{C} = 46.32$, $\text{H} = 7.16$, O (by diff.) = 46.52 per cent; (b) 1.5225 grms. dissolved in 33.58 grms. of ethyl alcohol raised the boiling-point by 0.245° (constant = 11.7); (c) a 10.94 per cent solution in ethyl alcohol at 18.6° gave $n_D + 3.023$ in a 400 m.m. tube (sp. gr. of solution 0.8251).
11. From what sources are glucose and lævulose prepared, and in what respects do they differ from one another? Give the constitutional formulæ of these sugars, and describe how one of them can be converted into the other.
12. Give an account of the reactions which nitrous acid yields with organic compounds. How would you ascertain whether a compound containing nitrogen and oxygen were a nitroso-derivative or not?

Practical Chemistry.

Wednesday, January 6th.

1. A is a solution of zinc and magnesium sulphates in water. Ascertain the amount of each in one litre of the solution.
2. Determine the melting-point of B (benzamide). To what type of compound does this substance belong?

Thursday, January 7th.

- A. Analyse qualitatively the given mixture. (Potassium tartrate, barium carbonate, magnesium phosphate; ammonium oxalate, cadmium carbonate, ammonium magnesium arsenate; sodium salicylate, aluminium phosphate calcium arsenate. One mixture given to each candidate)

B. Determine the percentage of potassium nitrate in the given solution by a gasometric method.

Friday, January 8th.

A is a solution of ammonium chloride and sulphuric acid in water. By means of the given semi-normal solution of sodium hydroxide determine the amount of ammonium chloride present. No other volumetric solution may be used.

B. The given mixture contains two organic substances. (Aniline hydrochloride and α -naphthol; aniline sulphate and β -naphthol. One mixture given to each candidate). Separate and identify them. Estimate their relative proportion in the mixture and prepare from each a characteristic derivative.

FINAL EXAMINATIONS FOR THE ASSOCIATESHIP.

Branch A—Mineral Chemistry.

Tuesday, January 12th.

Make a qualitative and quantitative analysis of the mixture A (lead oxalate, lead carbonate, and aluminium phosphate).

The estimation of one metal and of at least one acid radicle should be finished to-day, and the exercise completed to-morrow.

Wednesday, January 13th.

1. Complete the quantitative analysis of the mixture A given yesterday.

2. Ascertain what substances are present in the mixture B (ammonium persulphate and barium peroxide).

Thursday, January 14th.

1. Make an analysis of the sample of "furnace gas," and estimate the amount of each constituent.

2. Examine the given mineral C by the spectroscope and state what elements can be recognised in it (lepidolite).

Friday, January 15th.

1. The substance D is potassium nitrate with an admixture of a sulphite and sulphate. Find the proportion of potassium nitrate and estimate the amount of sulphite present.

2. Make a qualitative analysis of the mineral C examined spectroscopically yesterday.

Branch D.—Organic Chemistry.

Tuesday, January 12th.

1. What is the percentage of anthracene in the given sample of the crude hydrocarbon A? (This exercise may be completed to-morrow).

2. Identify the given substance B (benzenesulphonic chloride), checking your results by the quantitative determination of one constituent. Prepare specimens illustrative of the use to which the substance may be put in the laboratory.

Wednesday, January 13th.

The given liquid is a mixture of two substances (acetone and methyl alcohol). Identify them, determine their proportion in the mixture, and isolate one of them in a pure state. Leave specimens of any derivatives you are able to prepare.

Thursday, January 14th.

Prepare a litre of 3 per cent starch paste. Cool to 65° C., then add 25 c.c. of the given solution of malt diastase which has been previously raised to 65° C. Maintain the solution at this temperature and determine the reducing power, calculated as maltose, at stated intervals by means of a volumetric process. Plot your results on the squared paper supplied. Quantities of 50 c.c. should be withdrawn at intervals of 2, 4, 7, 10, 15, 30, 60, and 90 minutes, and

the diastatic action in each stopped by the addition of alkali.

Friday, January 15th.

1. The substance supplied is a commercial specimen of a base used in the manufacture of colouring matters (dimethylaniline containing monomethylaniline). Examine it, determine its nature, and report on its purity. Leave specimens of any derivatives you are able to prepare.

2. What do you consider to be the nature of the substance B? (Martius' yellow).

Branch E.—The Analysis of Foods and Drugs, and of Water.

Tuesday, January 5th.

Analyse the condensed milk, estimating the water, fat, proteids, and ash. From your results calculate the ratio between the original milk and the condensed product; state whether the sample is "skimmed."

Wednesday, January 6th.

1. Examine the honey by the polarimeter, and give an opinion as to whether the sample is adulterated with foreign sugars.

2. Find what ingredients have been added to the "self-raising" flour, and determine their amount.

Thursday, January 7th.

1. Identify the alkaloid in the given tincture (belladonna); estimate the quantity present, and state whether the tincture conforms to the requirements of the British Pharmacopoeia.

2. Test the given drugs for impurities and determine the proportion of any foreign ingredients. (Two samples given to each candidate).

Friday, January 8th.

1. Examine the water and report on its suitability for use in steam boilers. Give your opinion on the possibility of improving the water and state what treatment you recommend.

2. Write reports on the given samples. (Vinegar, lime-juice, and ginger wine. Two to each candidate).

Candidates in Branch E of the Final Examinations were required to pass an Examination in Therapeutics, Pharmacology, and Microscopy.

Saturday, January 9th.

1. Examine the specimen of mustard marked A, and report on its probable purity or otherwise, basing your opinion on the microscopical appearances only. Leave a prepared slide on your bench.

2. Examine by means of the microscope the specimen marked B. Describe in detail its nature as seen under the microscope. Leave a prepared slide on your bench.

3. Examine, describe, and state respectively the nature of the prepared slides marked C and D.

4. Mention the various metallic impurities that may be present in drinking waters. Describe the sources from which they are respectively derived, and briefly discuss the injurious effects that may be produced on the health of persons drinking such impure waters.

5. Give the full medicinal and the average fatal doses for an adult of the following substances:—Hydrocyanic acid (B.P.), phosphorus, acetanilide, chloral hydrate, croton oil, nitro-glycerin.

Candidates were also examined practically and interrogated orally as to the recognition of chemicals and drugs.

Examiners in Chemistry—Walter William Fisher, M.A. (Oxon.), F.I.C.; William Palmer Wynne, D.Sc. (Lond.), F.R.S., F.I.C.

Examiner in Therapeutics, Pharmacology, and Microscopy—Arthur Pearson Luff, M.D., B.Sc. (Lond.), F.R.C.P., F.I.C.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, January 20th, 1904.

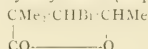
Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

(Concluded from p. 70).

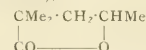
7. "The *cis*- and *trans*-Modifications of $\alpha\gamma$ -Trimethylglutaconic Acid." By WILLIAM HENRY PERKIN, jun., and ALICE EMILY SMITH.

The authors have already shown (*Trans.*, 1903, lxxxiii., 772) that when ethyl $\alpha\gamma$ -trimethylacetonedicarboxylate, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, is reduced with sodium amalgam, it is converted into a mixture of the *cis*- and *trans*-modifications of β -hydroxy- $\alpha\gamma$ -trimethylglutaric acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, and both of these, by treatment first with phosphorus pentachloride and then with diethylaniline, yield *trans*- $\alpha\gamma$ -trimethylglutaconic acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}=\text{CH}\cdot\text{CO}_2\text{H}$, which melts at 150° . They now show that on distillation both of the foregoing hydroxy-acids are converted into the anhydride of the *cis*-modification of $\alpha\gamma$ -trimethylglutaconic acid, which melts at 88° , and on hydrolysis yields the corresponding acid melting at about 125° . On treatment with bromine, *cis*-trimethylglutaconic acid yields *cis*- β -*γ*-dibromo- $\alpha\gamma$ -trimethylglutaric acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CHBr}\cdot\text{CHMeBr}\cdot\text{CO}_2\text{H}$, which melts at 168° .

During the distillation of the hydroxy-acids, a considerable amount of carbon dioxide and steam is eliminated, and an oily acid is produced which distils at 213° . This substance, *crotonyl dimethylglutaconic acid*, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}=\text{CHMe}$, when treated with bromine, yields the lactone of β -bromo- γ -hydroxy- $\alpha\gamma$ -trimethylbutyric acid (m. p. 83°),—



and, when boiled with dilute sulphuric acid, is converted into the lactone of γ -hydroxy- α - γ -trimethylbutyric acid (β -dimethylvalerolactone),—



which melts at 52° , and has already been described by Anschütz and Gillet (*Annalen*, 1888, ccxlvii., 107), who obtained it by the reduction of $\alpha\alpha$ -dimethylavulvic acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

8. "The Influence of Substitution in the Nucleus on the rate of Oxidation of the Side-chain. I. Oxidation of the Mono- and Dichlorotoluenes." By JULIUS BEREND COHEN and JAMES MILLER.

The method of oxidation adopted was to heat about a grm. of each of the isomerides with dilute nitric acid in a sealed tube for a length of time insufficient for complete oxidation and to estimate the proportion of the acid product and the unchanged substance. The vessel employed as air-bath was a jacketed, tin-plate cylinder containing boiling coal-tar naphtha, and furnished with a condenser, the tubes being heated in the inner compartment, which was kept at a nearly constant temperature.

The results of several series of experiments show that the monohalogen derivatives are more rapidly attacked than the dihalogen compounds. Of the three monochlorotoluenes, the meta-compound is least rapidly, and the para-isomeride most rapidly oxidised. Of the dihalogen compounds, the 3:5-compound is least affected; then follow the 2:5- and 2:6-isomerides, which are oxidised about equally; then the 2:3-compounds, and finally the 2:4- and 3:4-compounds, which may be bracketed together as being most readily attacked.

So far as these experiments are concerned, in which the oxidising agent is nitric acid, the results are perfectly

definite. The meta-compounds retard and the para-derivatives assist oxidation, whilst the ortho-compounds occupy an intermediate position.

Thus, *m*-chlorotoluene and 3:5-dichlorotoluene are least attacked by the acid, whereas *p*-chlorotoluene and the 2:4- and 3:4-dichlorotoluenes, which each contain a chlorine atom in the para-position with respect to the methyl group, are most rapidly oxidised.

9. "The Interdependence of the Physical and Chemical Criteria in the Analysis of Butter Fat." By THOMAS EDWARD THORPE.

In the course of an investigation on the chemical nature of butter produced within the British Isles, which was instituted by the Board of Agriculture for the information of a Departmental Committee appointed to report as to what regulations might with advantage be made for determining what deficiency in any of the normal constituents of butter should raise a presumption under the Food and Drugs Acts that the butter was not genuine, it became necessary to obtain at first-hand the values of butter of known origin and produced from milk given under varying conditions. Observation has shown that the chemical nature of butter fat is dependent, to a certain extent, on the climatic influences to which the cows are exposed, on the nature and amount of the food supplied, and on the breed, period of lactation, and idiosyncrasy of the individual cow. In order to give such weight as was practicable to the effect of these factors, the samples of butter were obtained from carefully selected districts, and often from cows set apart for the purpose of the inquiry, whilst particulars of the breed, diet, stabling, and period of lactation were supplied with the samples in nearly all cases. For example, to illustrate the effects of more rigorous climatic conditions than obtained in the United Kingdom generally, farms and dairies in Caithness, Sutherland, the Orkneys, Shetlands, and the Hebrides were laid under contribution, whilst a series of samples from Hollesley Bay, Suffolk, served to exemplify the effect on the cattle of exposure to the winds of the North Sea.

Of the 430 samples received, 357 were examined as regards their Reichert-Wollny number, their relative density, saponification value, and refractometric value, and in a certain number of typical cases their Hübl value was ascertained.

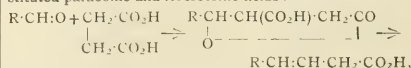
The main results of these observations have been tabulated and compared, and their interdependence exhibited by means of curves.

10. "A simple Thermostat for Use in Connection with the Refractometric Examination of Oils and Fats." By THOMAS EDWARD THORPE.

The thermostat is primarily intended for use in connection with the Zeiss butyro-refractometer, in which a current of water, usually at about 45° or a little warmer, is caused to circulate round the prism casing. This arrangement is somewhat more convenient than that usually employed, occupies less space, and is sooner brought into action. It has for some years past been employed in the Government Laboratory in the examination of butter.

11. "The Condensation of Furfuraldehyde with Sodium Succinate." By ARTHUR WALSH TITHERLEY and JAMES FREDERICK SPENCER.

Fittig has shown (*Annalen*, 1883, ccxvii., 97; 1889, cclv., 1—142) that aldehydes condense with sodium succinate in the presence of acetic anhydride, giving substituted paraconic and isocrotonic acids:—



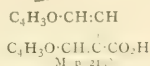
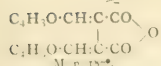
where R is any alkyl or aryl radicle.

The authors in attempting to employ this method for the synthesis of β furfurylidenepropionic (furfurylisocrotonic) acid by condensing furfuraldehyde with sodium succinate in presence of acetic anhydride, found that neither it nor

furfurylparaconic acid is formed, but two unexpected derivatives were produced, which were isolated with considerable difficulty, the yields being very small.

One of these substances, which crystallised in dark orange-coloured needles melting at 187° , was found to be difurfurylidene succinic anhydride, $C_{14}H_{10}O_4$, and the other, which separated in bright yellow plates (m. p. 213°), was identified as α -difurfurylidene propionic acid, $C_{13}H_{10}O_4$. These results indicated that two furfuraldehyde molecules condensed with one molecule of sodium succinate, and all attempts to prepare the corresponding monofurfurylidene derivatives failed.

These products may be regarded as being produced from the difurfurylidene derivative in the following manner:—



The orange-coloured anhydride is decomposed with difficulty by sodium hydroxide, forming sodium difurfurylidene succinate; the acid is a yellow, crystalline powder melting at 185 – 187° , and regenerating the anhydride. The acid is also converted into the anhydride on gently warming with acetyl chloride.

The anhydride readily combines with bromine, yielding the well-defined tetrabromide, α -B3-tetrabromo- α -difurfurylidene succinic anhydride,



a bright yellow powder melting at 166° , and giving fluorescent solutions.

The yellow α -difurfurylidene propionic acid (m. p. 213°) was obtained as the sole crystallisable product and in larger yield, on using succinic anhydride as the dehydrating agent instead of acetic anhydride, but in all cases the condensation of furfuraldehyde with sodium succinate was accompanied by the formation of large quantities of resinous matter.

12. "T₁. Action of Heat on α -Hydroxycarboxylic Acids." (A Preliminary Note). By HENRY RONDEL LE SUEUR.

The aldehyde, $C_{16}H_{33}CHO$, which is produced by heating α -hydroxystearic acid, crystallises from light petroleum in needles melting at 36° , and from alcohol in needles containing 1 mol. of the solvent, and melting at 52° ; it forms a crystalline compound with sodium hydrogen sulphite, and the oxime and semicarbazone melt at 89.5° and 107 – 108° respectively.

The acid, $C_{16}H_{33}CO_2H$, obtained by oxidising the aldehyde with potassium permanganate, crystallises from light petroleum in long needles melting at 60 – 61° ; the silver salt, $C_{17}H_{33}O_2Ag$, is amorphous.

The author is investigating the action of heat on other mono- and di-basic α -hydroxy-acids.

13. "The Fusion of Isopilocarpine with Caustic Potash." (A Correction). By HOOPER ALBERT DICKINSON JOWETT. In a communication on the constitution of pilocarpine (*Trans.*, 1900, lxxviii., 860), the author showed that an acid, then regarded as isobutyric acid, was produced by the fusion of isopilocarpine with caustic potash. The existence of the *n*-butyl group in isopilocarpine, as proved by the formation of α -ethyltricarballic acid from homopilocarpic acid, and the production of *n*-butyric acid by fusion of pilocarpic acid with caustic potash, however, rendered it probable that the acid previously described as isobutyric acid was really *n*-butyric acid. The experiment has therefore been repeated.

Ten grms. of isopilocarpine were fused with 100 grms. of caustic potash, and the fatty acid separated in the manner previously described (*loc. cit.*). The portion distilling between 120° and 160° was collected and converted into the calcium salt by neutralisation with calcium carbonate. The acid was not soluble in a small amount of water, but dissolved almost completely in a larger quantity. The calcium salt, which separated from the hot aqueous solution on concentration, was collected while hot; it formed white, pearly plates, which were dried in the air and analysed:

0.1982 lost 0.0162 H_2O at 150° . $H_2O = 8.2$.

0.1780 lost 0.0144 H_2O at 100° . $H_2O = 8.1$.

$(C_4H_7O_2)_2Ca \cdot H_2O$ requires $H_2O = 7.8$ per cent.

Calcium isobutyrate crystallises with 4 molecules of water.

On warming an aqueous solution of the salt, saturated at 0° , crystals separated, which re-dissolved on cooling.

The silver salt was prepared and re-crystallised from water.

0.1412 gave 0.0726 Ag. Ag = 55.3.

$C_4H_7O_2Ag$ requires Ag = 55.4 per cent.

The volatile acid formed by the fusion of isopilocarpine with caustic potash is therefore *n*-butyric acid.

14. "Organic Derivatives of Silicon. Preparation of Alkylsilicon Chlorides." By FREDERIC STANLEY KIPPING.

It has been previously shown that tetra-alkyl derivatives of silicon can be obtained by treating silicon tetrachloride with alkyl halides in presence of sodium (Kipping and Lloyd (*Trans.*, 1901, lxxix., 449)). The investigation of silicon compounds has recently been resumed in conjunction with Mr. A. Hunter, and attempts have been made to prepare compounds of the type $SiR_1R_2R_3Cl$ with the following results:—

Silicon tetrachloride interacts vigorously with an ethereal solution of magnesium ethyl iodide, the product consisting of a mixture of ethylsilicon trichloride, diethylsilicon dichloride, triethylsilicon chloride, and silicon tetraethyl, the proportions of which depend on the relative quantity of the magnesium compound employed.

Silicon tetrachloride also interacts very vigorously with an ethereal solution of magnesium ethyl bromide; when molecular proportions of the two compounds are used, the product contains a small quantity of the di- and tri-ethyl derivatives, but consists principally of ethyl silicon trichloride, which can be isolated by fractional distillation and has the properties assigned to it by Ladenburg.

Ethylsilicon trichloride and an ethereal solution of magnesium phenyl bromide interact very readily, and phenylethylsilicon dichloride can be isolated by fractional distillation; this compound is a fuming liquid boiling at about 228 – 230° , and readily decomposed by water, giving an oil which appears to be the silicoketone, $SiEtPhO$.

Phenylethylsilicon dichloride and an ethereal solution of magnesium propyl bromide do not give an immediate precipitation of magnesium salt, but on warming, a reaction occurs with the formation of phenylethylpropylsilicon chloride, which is obtained after fractional distillation, mixed apparently with unchanged dichloride, as a colourless liquid boiling indefinitely at about 240° .

These and other alkyl derivatives of silicon tetrachloride are now being examined, and, in conjunction with Dr. Caven, analogous experiments have been commenced with the object of preparing mixed alkyl derivatives of phosphorus, more especially compounds of the type $POR_1R_2R_3$ or POR_1R_2OH .

15. "Derivatives of Highly Substituted Anilines." By FREDERICK DANIEL CHATLAWAY and JOHN MELLO WADMORE.

The authors described the preparation and properties of a series of highly substituted acyl- and chloro-amines obtained in the course of an investigation into the phenomena of intramolecular re-arrangement in aromatic amines.

CORRESPONDENCE.

ESTIMATION OF THE ADULTERANT IN
CITRONELLA OIL.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of January 8, 1904 (vol. lxxxix., p. 27), there is an article by M. K. Bamber on the "Estimation of the Adulterant in Citronella Oil." I would like to know where the tubes there described may be obtained, and if the specific gravity of the alcohol, ρ_{8273} at 30° C., is referred to water at 15° C. in air as unity.—I am, &c.,

WILSON H. LOW.

Chemist of the Cudahy Packing Co.

The Cudahy Packing Co., South Omaha, Neb.
January 22, 1904.

THEORY OF ELECTROLYTIC DISSOCIATION.

To the Editor of the Chemical News.

SIR,—As already stated a few weeks back, I propose shortly to contribute, with your permission, a few pages on the nature of the liquid state, and the position I shall therein take up is one diametrically opposed to the theory advocated in Mr. Joseph W. Richards's recent paper (CHEMICAL NEWS, vol. lxxxix., pp. 31, 37).

But meanwhile, lest your readers should be over-impressed by the calculations which form the sole appeal made by Mr. Richards to experimental facts, permit me to offer a few remarks in criticism of the same.

It is certainly a very remarkable coincidence that the concentration used by Thomsen in the determination of the heat of neutralisation of caustic soda by hydrochloric acid should be just the one which favours Mr. Richards's theory. Yet so it is, and a little consideration will show that with any other concentration his figures totally fail.

To prove this, I must quote his calculations pretty fully. He contends that, according to his theory, the heat of neutralisation must be equal to the heat of vapourisation of liquid water at the given temperature, so as to form gaseous water at the same temperature and under an osmotic pressure equal to that due to the "ionised water," from which he assumes it is formed. The temperature is 18°, and the osmotic pressure of "ionised water" under the conditions of concentration assumed by Thomsen would be, as Mr. Richards shows, about 6.19 atmospheres. He uses this pressure to calculate the total work of vapourisation, taking the heat of vapourisation less the "outer work" as 10,110 calories (obtained quite legitimately from Regnault's figures), and adding thereto the outer work $6.19 \times$ the thermal factor $2 \times T$. Thus he obtains the number $10,110 + 6.19 \times 2 \times T = 10,110 +$ (not $\times$ as misprinted) $3590 = 13,700$ calories. Now the heat of neutralisation is 13,740 calories. Q.E.D.

Yes, but let us assume another concentration. Let us take instead of Thomsen's concentration a solution ten times as dilute. Now, everybody knows well enough that Thomsen used a dilution so great that further dilution made practically no thermal difference. At this greater dilution, then, the heat of neutralisation will still be 13,740. But the osmotic pressure above referred to must be reduced to $\frac{1}{10}$; it is now only 0.619 atmosphere, and according to Mr. Richards's calculation the result will come out $10,110 + 0.619 \times 2 \times T = 10,110 + 3.59 = 10,114$ calories. So much for Q.E.D.

And then again in his next calculation he uses this same quantity (less one atmosphere in his product), viz., $(6.19 - 1) \times 2 \times T = 3021$ calories, to add to his calculated number 55,200 in order to make the result come out to 58,221 calories, and thus tally with the molecular heat of formation of water gas from oxygen and hydrogen which, as deduced from Regnault, is 58,100 calories.

But under the circumstances of greater dilution as above, the osmotic pressure is not 6.19 atmospheres but 0.619, and the quantity to be added will be negative, viz., $(0.619 - 1) \times 2 \times T = -0.381 \times 2 \times T = -222$. The result instead of 58,100 is 54,978. And with other concentrations of course other variations occur. In fact, by diminishing the concentration and increasing the temperature, you can gradually make the number 55,200 to vanish. Thus does the sole experimental proof of the theory for which such an imposing array of tabulated figures are deduced collapse like a house of cards.

Mr. Richards's theory is originated, he tells us, to account for the fact that that one molecule of a salt (say KCl) cannot be ionised (into two molecules K, Cl) without enormous thermal disturbance. But if this is any difficulty it is entirely balanced by the fact that the electrolytic decomposition of the ionised KCl into free potassium and free chlorine takes place practically without any expenditure of work. That is a fact really quite inexplicable on Mr. Richards's theory, so he only surmounts one difficulty to raise another. If the point he refers to is really difficult, the difficulty readily vanishes on consideration of the enormous tensions (not osmotic but due to intermolecular attraction), hundreds of atmospheres, which exist between the molecules of the solvent, and the mechanical changes in these tensions, resulting from the introduction of the solute, are quite sufficient to account for the disappearance of the heat of decomposition of the salt into its ions.

There is another point, however. If the ionised salts are, as Mr. Richards says, still compounds, then since, as he points out, they have the properties of a gas (even the osmotic coefficient agreeing with the gas coefficient), how comes it that an ionised binary molecule, such as KCl, poses as two gas molecules in its osmotic pressure and not as one?—I am, &c.,

P. J. BEVERIDGE, M.A., B.Sc.

7, Bridge Place, Chester,
February 1, 1904.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxviii., No. 2, January 11, 1904.

Colour Reactions of Vanadic Acid and Ethenol.—Camille Matignon.—Whilst investigating a method of colour estimation of vanadic acid the author discovered a number of facts about the properties of this acid. Tannin gives a dark blue precipitate or a colouration of the same tint with solutions of ammonia metavanadate when fairly dilute, and the author finds that gallic and pyrogallol acid with vanadic solutions also give very dark blue colourations. He also makes various experiments on certain active ethers and their effects on vanadic acid.

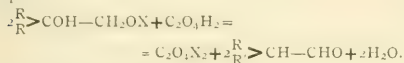
Use of Bismuth as a Separating Agent in the Series of the Rare Earths.—G. Urbain and H. Lacombe.—Already inserted in full.

New Method of Estimation of the Halogen Elements in Organic Bodies. Chlorine and Bromine.—H. Baubigny and G. Chavanne.—In a previous research the authors investigated a method of estimation of iodine in organic compounds, based on the destruction of the substance by a chromosulphuric mixture and the transformation of the iodine into fixed iodic acid. It is evident that the same method of combustion can be applied to bodies containing chlorine and bromine, but the method fails when the oxidation of the chlorine or bromine is attempted. However, they describe, with a drawing, an apparatus by which the quantitative estimation of the chlorine and bro-

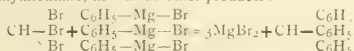
mine, after the destruction of the organic matter, can be accurately determined.

Titration of Manganese.—Léon Débourdeaux.—The titration of manganese oxides necessitates two determinations:—(1) That of the chlorine which the oxide can set free; (2) that of the hydrochloric acid necessary to set free all the chlorine which is present. These two estimations, which usually need two distinct operations, can be effected in a single experiment by a method founded on the destruction of the superior oxides of manganese by hot oxalic acid in presence of suitably diluted sulphuric acid. This method has the advantage of needing very little attention. The two determinations of the titration take place rapidly and exactly in a single experiment. It is applicable to all manganese salts without previous elimination of the carbonates.

A Method of Synthesis of Aldehydes.—MM. Béhal and Sommelet.—The authors find that the aldehydes $(R)_2CH=CHO$ and $\frac{R}{R'}>CH=CHO$ can be obtained from the ether oxides of the α -glycols corresponding to the formulæ $\frac{R}{R'}>COH-CH_2OX$ and $\frac{R}{R'}>COH-CH_2OX$ by decomposition with dry oxalic acid. In these formulæ, X represents an alcoyl or a monovalent aromatic radical. The transformation is effected according to the following equation:—



Synthesis of Aromatic Aldehydes.—F. Bodroux.—Iodoform and bromoform act energetically on organomagnesium compounds at ordinary temperatures. In the case of phenylmagnesium bromide the author obtained triphenylmethane, as well as other products:—



The yield in this case was not good, so he replaces the halogen derivatives by ethyl-ortho-formate, and, at the temperature of a water-bath after six hours, a considerable quantity of benzylic aldehyde is produced.

Active Influence of Albumenoid Matter on Oxidation by means of Manganese.—A. Trillat.—The author's experiments show that albumin has the property of preventing the precipitation of manganese dioxide even in presence of a strong alkali. If a solution of a manganese salt and an alkali are successively added to a dilute solution of albumin the liquid becomes slightly brown, but no precipitate forms; if, on the contrary, there is no albumin, an abundant precipitation takes place.

MISCELLANEOUS.

Some Constants of Sulphide of Carbon.—V. Unruh.—The sulphide is purified by treating 500 to 700 c.c. with 6 to 8 c.c. of pure dry mercury and porous CaCl_2 . Shake, filter, and distil in the dark. This operation is repeated until no more sulphide of mercury is formed. The first portions (15 to 20 per cent) and the last portions (10 to 15 per cent) are set on one side, and treated again like the impure sulphide. The pure product has an ethereal odour, and its boiling-point is constant to about $0^{\circ}002^{\circ}$; this is contrary to the results found by Arctowsky (*Zeit. Anorg. Ch.*, vol. vi., p. 255). A variation of 1 m.m. in the atmospheric pressure causes a variation of $0^{\circ}04144^{\circ}$ in the boiling-points. At a boiling-point of $46^{\circ}25'$, the density = 1.2209 . This density varies considerably when the boiling takes place under pressures slightly different from the atmospheric pressure. For example, at 756.6 m.m., and with a boiling-point of $46^{\circ}10'$, the density = 1.22161 .—*Zeit. Anorg. Ch.*, vol. xxxii., p. 407.

Institute of Chemistry Examinations.—Pass Lists (January, 1904).—*Intermediate Examination*: Stanley Winter Collins, King's Coll., London; David Cowan Crichton, Univ. Coll., Dundee; Harold Deane, B.Sc. (Lond.), School of the Pharmaceutical Society, London; Cyril Dickinson B.Sc. (Vict.), Yorkshire Coll., Leeds; John Augustus Goodson, Finsbury Tech. Coll., London; Henry Ward Goodwin, Univ. Coll., Nottingham; Alfred George Holborow, Merchant Venturers' Tech. Coll., Bristol, and Glasgow and W. of Scot. Tech. Coll.; Charles James, Univ. Coll., London; Harry Edwin Laws, Univ. Coll., Nottingham; Robert Park, King's Coll., London, and under J. Falconer King, F.I.C.; Edwin Rhodes, B.Sc. (Vict.), Yorkshire Coll., Leeds. *Final A.I.C. Examination—Branch "A" (Mineral Chemistry)*: Denison Benzeville Byles, Univ. Coll., London; Arthur Charles Carter, Univ. Coll., London; James Gray, Glasgow and W. of Scot. Tech. Coll.; Arthur Hopwood, Assoc. R.C.Sc. (Lond.), Royal Coll. of Science, London. *Branch "D" (Organic Chemistry)*: Marmaduke Barrowcliff, Univ. Coll., Nottingham; Edwin Jesse Fairhall, A.C.G.I., Central Tech. Coll., London; William Oswald Littlebury, Univ. Coll., Nottingham; Miss Frances Mary Gore Micklethwait, Assoc. R.C.Sc. (Lond.), Royal Coll. of Science, London; Fred. Scholefield, B.Sc. (Lond. and Vict.), Yorkshire Coll., Leeds; Harold Stevenson, Univ. Coll., Nottingham. *Branch "E" (Analysis of Food and Drugs and of Water, including Examination in Therapeutics, Pharmacology, and Microscopy)*: James Handby Ball, B.Sc. (Vict.), Univ. Coll., Liverpool; Herbert Sutcliffe Shrewsbury, Univ. Coll., Nottingham; Henry Edgar Watt, M.Sc. (Durham), Durham Coll. of Science, Newcastle-on-Tyne. *For the Fellowship (F.I.C.)—Branch "D" (Organic Chemistry)*: Harold Hibbert, M.Sc. (Vict.), Owens Coll., Manchester, and Univ. Coll., Aberystwyth. *Branch "E" (Analysis of Food and Drugs and of Water, including Examination in Therapeutics, Pharmacology, and Microscopy)*: Edward William Lucas, School of the Pharmaceutical Society, London.

Organo-metallic Compounds of Benzoic Acid.—L.

Pesci.—*o*-Oxymercuribenzoic Anhydride, $\text{C}_6\text{H}_4\text{CO}_2\text{Hg}$.—This substance is obtained by heating a mixture of 32 parts of acetate of mercury and 20 parts of benzoic acid to about 140° . The mass is dissolved in a boiling solution of Na_2CO_3 , and the solution precipitated with CO_2 ; the precipitate dissolved in ammonia gives the ammonium salt in a well crystallised form; this is decomposed by dilute acetic acid. It is also obtained by boiling acetate of mercury with phthalate of soda and a little acetic acid. CO_2 is given off, and the mercury is substituted for the ortho, CO_2H . It is an insoluble white powder, decomposed by the mineral acids. When strongly heated it deflagrates, Salt of Ammonium, $\text{HO}-\text{C}_6\text{H}_4-\text{CO}_2\text{NH}_4$.—Needles, slightly soluble in water in the cold, dissociated by heat, returning to the anhydride. The salt of barium is obtained from $\text{Ba}(\text{OH})_2$ and the anhydride. It occurs in needles, soluble in water, decomposed by CO_2 . The salts of calcium, magnesium, isoamylamine, and benzylamine are also formed. *o*-Chloromercuribenzoic Acid, $\text{C}_6\text{H}_4\text{ClCO}_2\text{Hg}$.—This is a microcrystalline powder, slightly soluble in water, obtained by precipitating one of the preceding salts with acetic acid in the presence of a large excess of a soluble chloride. The salt of potassium, $\text{C}_6\text{H}_4(\text{HgCl})(\text{CO}_2\text{K})14\text{H}_2\text{O}$, is obtained in brilliant needles by the saturation of a hot solution of KCl with mercurio-benzoic anhydride; it is deposited on cooling; it loses its water at 100° , and is decomposed by hot water. There are also formed the salt of soda with $24\text{H}_2\text{O}$; the salt of ammonium crystallised with $2\text{NH}_4\text{Cl}$; the salt of barium with $3\text{H}_2\text{O}$, and the salt of aniline. *o*-Bromomercuribenzoic Acid, $\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{HgBr})$.—The salt of potassium, the salt of sodium with $3\text{H}_2\text{O}$, and the salt of barium with $3\text{H}_2\text{O}$ are all prepared as in the preceding cases. *a*-Iodo-

mercuriobenzoic Acid.—This forms anhydrous salts of potassium, sodium, and barium. The Salts of *o*-Sulpho-mercuriobenzoic Acid, $S:(Hg.C_6H_4.CO_2H)_2$.—The salt of sodium is obtained by the action of 1 molecule of Na_2S on 2 molecules of mercuriobenzoate of soda. The precipitate consists of white needles. Acetic acid gives a gelatinous mass; the salt of potassium is in needles, soluble in water. *o*-Mercuriodibenzoic acid, $Hg:(C_6H_4.CO_2H)_2$, obtained by the prolonged boiling of one of the preceding sulpho-salts with water, HgS is produced, and the corresponding salt of the acid. Acetic acid decomposes this salt and precipitates the free acid, which is crystallised in boiling alcohol. It occurs in colourless needles decomposed by heat. The salt of potassium is in needles soluble in water; that of sodium is slightly crystalline; that of ammonium occurs in rhombohedra slightly soluble in water, and that of calcium is insoluble in water.—*Gazz. Chim. Ital.*, [2], vol. xxxii., p. 277.

MEETINGS FOR THE WEEK.

MONDAY, 15th.—Society of Arts, 8. "Cantor Lectures," "Oils and Fats—their Uses and Applications," by J. Lewkowitch, Ph.D., &c.

TUESDAY, 16th.—Royal Institution, 5. "Development of Animals," by Prof. L. C. Miall, F.R.S.

WEDNESDAY, 17th.—Society of Arts, 8. "Garden Cities in their Relation to Industries and Agriculture," by A. R. Senoett.

Chemical, 5.30. "Observations on some Continuous Intramolecular and at first Reversible Changes extending over Prolonged Periods of Time," by R. J. Friswell. "The Esterification of γ -Mandelic Acid by Menthol and Borneol," by A. McKenzie.

Microscopical, 8. "On the Vertical Illuminator" and "The Influence of the Anti-point on the Microscopic Image shown Graphically," by E. M. Neilson. "A Microscope with Geometric Slides," by Keith Lucas. Mr. C. L. Curties will exhibit Specimens of Marine Objects mounted by Mr. H. J. Wadington.

THURSDAY, 18th.—Royal Institution, 5. "Recent Research in Agriculture," by A. D. Hall, M.A.

FRIDAY, 19th.—Royal Institution, 9. "Condensation Nuclei" (Illustrated by Experiment), by C. T. R. Wilson, F.R.S.

SATURDAY, 20th.—Royal Institution, 3. "The Life and Work of Stokes," by Right Hon. Lord Rayleigh, F.R.S.

THE ROYAL WATERLOO HOSPITAL FOR CHILDREN & WOMEN,
WATERLOO BRIDGE ROAD, S.E.

There is a vacancy for a fully qualified HEAD DISPENSER at the above Institution. Applications can only be entertained from those in possession of the Pharmaceutical Society's qualifications.

Particulars may be obtained from the SECRETARY at the Hospital, to whom applications, with testimonials, &c., must be forwarded on or before FEBRUARY 23rd.

THE CHEMICAL NEWS AND JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free (including Indices, £1).

CHARGES FOR ADVERTISEMENTS.

Five lines in column (about 10 words to line)	4 s. d.
Each additional line	0 3 6
Whole column	0 0 6
Whole page	1 15 0
Whole page	3 0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed ("London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

BIRKBECK COLLEGE

(BIRKBECK INSTITUTION),
Breems Buildings, Chancery Lane, E.C.

DAY AND EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, AND ASSAYING	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board, Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.

INSTRUCTION IN

PURE CULTIVATION OF YEAST. According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeast brewers' distillers', wine, disease yeasts, moulds, and bacteria. *Manuals*: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jørgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufacturers, &c.

Further particulars on application to the Director—
ALFRED JØRGENSEN, The Laboratory, Copenhagen, V.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1s. 6d. each.

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

LEWIS'S MEDICAL AND SCIENTIFIC LIBRARY.

SUBSCRIPTIONS FROM ONE GUINEA.

Detailed Prospectus and List of New Books post free on application.

London: 136, Gower Street, W.C.

MARTINDALE'S Apparatus and Reagents

For Chemical and Bacteriological Research.

SPECIALITIES:—

MARTINDALE'S BURETTE STAND 9/-, 15/-
MARTINDALE'S BACTERIOLOGICAL CASE 42/-

Analytical Price List post free. Telephone—1797 Paddington.

W. MARTINDALE, 10, New Cavendish St., W.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC, As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, &c.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2308.

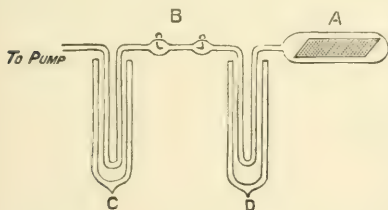
EXAMINATION OF A SAMPLE OF GAS OCCLUDED IN RADIUM BROMIDE.*

By Professors CURIE and DEWAR.

THE sample of radium bromide amounting to 0.42 gm. had been prepared about three months, and was brought to the Royal Institution for the purpose of continuing the enquiry on the heat evolution at the temperature of boiling hydrogen. It contained some water of hydration, and had been giving off permanent gas amounting to about 1 c.c. per month while kept in a chamber that had been previously highly exhausted. This gas, examined in the spectroscope, appeared to be chiefly hydrogen.

It was now determined to transfer the specimen of the radium bromide to a quartz tube, so that it might safely be exhausted to the limit of a mercurial vacuum during the fusion of the salt above a red heat. By introducing two or three small U-tubes immersed in liquid air between the pump and the quartz tube containing the salt, all mercurial vapour was prevented from access to the quartz tube, while water, together with traces of bromine or carbonic acid, and the emanation given off during the heating, were separated and condensed. At the same time any permanent gas passing the liquid air condensers, along with the more volatile part of the emanation pumped out during the continuance of the high exhaustion, was collected after passing through the mercurial pump.

Having exhausted the radium bromide for some hours at the ordinary temperature until no further trace of gas came off, it was gradually heated to fusion. During the heating, gas came off rapidly, the total quantity collected amounting to 2.6 c.c. (in all probability not less than thirty times the volume of the fused radium bromide). After the elimination of gas from the fused radium bromide had ended, the small piece of quartz tube, containing now about 0.4 gm., was sealed off by means of the oxy-hydrogen blow-pipe, the intention being to examine it later on spectroscopically.



The gas that came through the mercurial pump was transferred to a small mercury burette, and as it was so luminous and powerfully radio-active it was put away in a dark room for the purpose of taking a photograph of its spectrum. On developing the plate after three days' exposure (during which time the walls of the glass tube containing it had become deep violet and nearly half the volume of gas absorbed) it was found to reveal a discontinuous spectrum, consisting of three bands coincident with the nitrogen bands λ 3800, 3580, and 3370. This is a remarkable result considering

the amount of the emanation present could only be small, being such as was volatile at the temperature of liquid air.

The part of the eudiometer where the luminous gas had stood over mercury was cut off. The glass was deep violet all through the mass, and the surface was covered in parts with what looked like some mercury compound. This piece of tube was placed inside a closed tube, A, of hard glass, which was sealed on to a vacuum tube, B, with small U-tubes, c and d, on each side for cooling in liquid air.

After thorough exhaustion the part A was heated to a low red heat, so that the violet coloured piece of tube covered with the mercury compound might be decomposed and any permanent gaseous product collected in a glass vacuum tube, while vapour of water, carbonic acid, and mercury vapour were all condensed in the liquid air U-tubes. The result of the heating was to make the glass lose its violet colour and to increase the pressure in the sparking tube from the gas given off during the heating. The vacuum tube was afterwards sealed off from the U-tubes and spectroscopically examined. This gas gave the spectrum of nitrogen, no hydrogen being visible.

To confirm the composition of the gas, occluded by the radium bromide, that portion which had not been absorbed while standing over mercury was transferred to a highly exhausted spectroscopic tube having a narrow side tube attached that could be cooled in liquid hydrogen and then sealed off. In the transference of the gas and exhaustion of the vacuum tube, liquid air U-tubes to condense impurities and keep out mercurial vapour were employed.

On passing the electric discharge, the spectrum emitted was solely that of the nitrogen band spectrum, no other lines being visible. When the side tube was placed in liquid hydrogen the nitrogen rapidly condensed, and the vacuum became very high. After the condensed material in the side tube was sealed off, the vacuum tube showed a hydrogen spectrum, and nothing else. In such a tube it would be impossible to find small amounts of helium by the spectroscope, seeing that a 10 per cent helium-hydrogen mixture shows nothing but hydrogen.

The most hopeful anticipation of a knowledge of the character of the gases given off during the transitions taking place in radium bromide was clearly to make a spectroscopic examination, after keeping for some time, of any gaseous atmosphere developed in the carefully exhausted quartz tube, and this M. Deslandres has done, with the result that the internal gas, illuminated by an induction spark through two pieces of tin-foil covering the two ends of the tube, gave the entire spectrum of helium. No lines except those of this gas were discovered after an exposure of three hours in a quartz photographic spectroscope.

Until the full spectroscopic examination by Deslandres is published no inference can be drawn as to whether or no the amount of helium has gone on increasing in the quartz tube (as it ought to do if it is a true product of the disintegration of radium) and no conclusion drawn as to the presence of other gases and their origin, whether new or old.

During the discussion of radio-activity at the last meeting of the British Association, an account was given of some experiments made by Prof. Dewar and Sir William Crookes on the spectrum given by radium bromide when sealed up in quartz tubes, in the first instance when exhausted, and, secondly, when filled with helium at different pressures. In neither case did a discontinuous spectrum result. If the gas in presence of the radium bromide was, however, air, the nitrogen bands appeared under exactly the same conditions, thus confirming the observations of Sir W. and Lady Huggins. It is an interesting fact that the radiations should not be able to excite the helium atom to vibration, whilst this result is easily attained in the case of nitrogen. Further, helium at atmospheric pressure seem to be the gas of all others that most easily conducts electric discharges. This matter requires further investigation.

* Translated from the *Comptes Rendus*, vol. CXXXVIII., p. 190, with emendations.

ON THE COMPRESSIBILITIES OF OXYGEN,
HYDROGEN, NITROGEN, AND CARBONIC OXIDE
BETWEEN ONE ATMOSPHERE AND
HALF AN ATMOSPHERE OF PRESSURE,
AND ON THE ATOMIC WEIGHTS OF THE
ELEMENTS CONCERNED.*

(PRELIMINARY NOTICE).

By Lord RAYLEIGH, O.M., F.R.S.

THE observations now referred to were conducted with an apparatus designed upon the same lines as that already described ("On the Law of the Pressure of Gases between 75 and 150 m.m. of Mercury," *Phil. Trans.*, A., 1902, vol. 198, pp. 417-430). It must suffice to mention that the only important modification lay in the fact that the two single volumes, which, when employed together, constitute the double volume, were used separately and alternately, so as to eliminate in each set of measurements any question as to what the ratio of these volumes exactly is. It is hoped to give a full description of the method when it has been extended to the examination of other gases, such as nitrous oxide and carbonic anhydride. The temperatures ranged from 10° - 15° , and care was taken that in each measurement the mean temperatures should be almost exactly the same for the single and for the double volume.

The results were reduced much as previously explained, and give for the values of B, which, according to Boyle's law, should be unity:—

Oxygen	1'00040
Hydrogen	0'99976
Nitrogen	1'00017
Carbonic oxide .. .	1'00028

B here denotes the quotient of the value of p_v at the half atmosphere by the corresponding value at the whole atmosphere. That it would be less than unity in the case of hydrogen, and exceed unity for the other gases, is what would be anticipated from their behaviour at higher pressures.

If we measure p in atmospheres, and assume, as has usually been done, e.g., by Regnault and Van der Waals, that at small pressures the equation of an isothermal is:—

$$pv = PV(1 + ap),$$

where PV is the value of the product in a state of infinite rarefaction, then:—

$$a = 2(1 - B).$$

Probably the chief interest of a knowledge of the coefficient a is the application to deduce a correction to the relative densities of gases as observed at atmospheric pressure, so as to determine what would be the relative densities in a state of great rarefaction, to which alone Avogadro's law is applicable. (The application to oxygen and hydrogen was made in my paper, "On the Relative Densities of Oxygen and Hydrogen," *Roy. Soc. Proc.*, 1892, vol. 1, p. 448; "Scientific Papers," vol. iii., p. 525).

Taking oxygen as a standard, we see that the small correcting factor to be introduced in order to pass from the ratio of densities at one atmosphere to that at great rarefaction, is $(1+a)/(1+a_0)$, or $1+2(B_0-B)$, the suffix 0 relating to oxygen, that is, as follows:—

Hydrogen	1'00128
Nitrogen	1'00046
Carbonic oxide .. .	1'00024

The double of the first number, viz., 2'0026, represents, according to Avogadro's law, the volume of hydrogen which combines with one volume of oxygen at atmospheric pressure to form water. Direct determinations by Scott gave 2'00245, and Morley, in his later work, found 2'0027, so that there is here a good agreement.

The following table gives the densities of the various gases, referred to oxygen = 16, at atmospheric pressure and at very small pressure, as deduced from my own observations (*Roy. Soc. Proc.*, 1893, vol. liii., p. 134; 1897, vol. lxii., p. 204; "Scientific Papers," vol. iv., pp. 39, 352):—

Gas.	Atmospheric pressure.	Very small.
Hydrogen	1'0075	1'0088
Nitrogen	14'009	14'009
Carbonic oxide .. .	14'000	14'003

From the researches of M. Leduc and Prof. Morley, it is probable that the above numbers for hydrogen are a little, perhaps one thousandth part, too high.

The uncorrected number (14'003) for nitrogen has already been given (Rayleigh and Ramsay, *Phil. Trans.*, A., 1895, vol. clxxvi., p. 187), and contrasted with the 14'05 obtained by Stas. This question deserves the attention of chemists. If Avogadro's law be strictly true, it seems impossible that the atomic weight of nitrogen can be 14'05.

From the molecular weight of CO, viz., 28'006, we deduce, as the atomic weight of carbon, 12'006.

It should be mentioned that D. Berthelot (*Comptes Rendus*, 1898) has, meanwhile, calculated very similar numbers, based upon the observations of Leduc.

ON CERTAIN PROPERTIES OF THE
SILVER-CADMIUM SERIES OF ALLOYS.*

By T. KIRKE ROSE, D.Sc.

THE attempts made at the Royal Mint to produce uniform standard trial plates of silver and copper have been unsuccessful owing to the segregation of the constituents. The cooling curve of the alloy shows that solidification begins at 900° and ends at 778° , after passing through a pasty stage, during which rearrangement of the constituents can take place, with the result that the uniform distribution of the silver is disturbed. The cooling curve of the alloy containing 92'5 per cent of silver and 7'5 per cent of cadmium is found to resemble that of a pure metal, showing no appreciable pasty stage, and on testing plates made of these materials, they were found to be uniform in composition. The alloy is exceedingly ductile, and no difficulty is encountered in making assays on it by any of the well-known methods. In preparing large ingots it is necessary to pour silver into a suitable amount of molten cadmium, this method minimising the loss of cadmium by volatilisation.

The cooling curves and the microstructure of the whole series of alloys of silver and cadmium have also been studied, and evidence has been obtained of the existence of a number of compounds. The curves of equilibrium of the series are complicated by the effects of the compounds. The alloys containing from 100 to 80 per cent of silver are homogeneous at all temperatures below the solidus curve, although they appear to contain two bodies between the solidus and liquidus curves. There is a well-marked cusp in the curves, corresponding to the compound Ag_2Cd_3 and an alloy of minimum freezing point containing about 1 per cent of silver. Among the alloys containing less than 80 per cent of silver, only those corresponding in composition to the formulae Ag_2Cd , $AgCd$, Ag_2Cd_3 , and $AgCd_3$ appear to be homogeneous.

Synthesis of Sugars from Trioxymethylene and Sodium Sulphite.—A. Seyewetz and M. Gibello.—The authors transform trioxymethylene dissolved in a solution of sodium sulphite into sugar derivatives. No appreciable transformation takes place at ordinary temperatures, but sugar compounds begin to be formed directly the solution is heated on the water-bath, and more rapidly still when boiled.—*Comptes Rendus*, cxxviii., No. 3.

* A Paper read before the Royal Society, February 11, 1904.

* Abstract of a Paper read before the Royal Society, Feb. 1 1904.

THE PRODUCTION OF CRYSTALLISED SALTS OF BISMUTH.

By A. DE SCHULTEN.

Sub-nitrates of Bismuth.

In undertaking the examination of these salts, which have been already the subject of research by numerous writers, I have limited the field of my inquiry at first to the crystalline compounds which are produced by the action of water in the cold on a solution of nitrate of bismuth in nitric acid.

The Salt $5\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$.—I dissolved 50 grms. of the salt $\text{Bi}(\text{NO}_3)_3 + 5\text{H}_2\text{O}$ in 50 c.c. of nitric acid of 1·2 density, and added 3 litres of water while stirring. After twelve hours I collected the crystals produced by this reaction on a filter, and pressed them between filter-papers with great care. The crystals are air-dried until their weight no longer changes. During this desiccation the crystals do not undergo any change. They retain their form and limpidity, and their facets, though striated, always remain smooth.

On analysis the crystals give the following figures:—

	Found.			Calculated for $5\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$.
	I.	II.	III.	
Bi_2O_3	76·83	76·83	76·84	76·79
N_2O_5	17·82	—	—	17·85
H_2O (by diff.)	5·35	—	—	5·36
	100·00			100·00
Calculated for—				
	$4\text{Bi}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$.			$6\text{Bi}_2\text{O}_3 \cdot 6\text{N}_2\text{O}_5 \cdot 11\text{H}_2\text{O}$.
Bi_2O_3	76·91	76·72	76·34	
N_2O_5	17·88	17·83	17·74	
H_2O	5·21	5·45	5·92	
	100·00	100·00	100·00	

The oxide of bismuth was estimated by calcining the material, and the nitric acid by Pelouze's method. In Analysis I. the oxide of bismuth was estimated on 12·87 grms. of material; in Analysis II. on 8·04 grms. of material from another preparation. In Analysis III. the bismuth was estimated on 3·78 grms. of material. For this analysis I prepared the substance in the manner just described, with the exception that I precipitated the solution of nitrate of bismuth with only 1·75 litres of water instead of 3 litres, and I collected the crystals immediately after their formation. In this manner I proved conclusively that the contact of the crystals with the mother-liquor for twelve hours did not cause any partial decomposition.

The figures furnished by the analyses do not agree, as will be easily seen, with those calculated for the simple formula $5\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$, generally accepted for the sub-nitrate of bismuth obtained under the conditions in which I operated. The formula which represents their composition the best is $5\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$.

When placed over sulphuric acid the crystals lose water. After forty days their weight remained constant. The loss of weight amounted to 3·14 per cent, corresponding to 5·27 molecules of water.

The crystals have a pearly lustre. They take the form of very thin plates, hexagonal in form, and more often slightly elongated. They are striated parallel with the elongation. Extinction takes place at an angle of about 13° with the elongation. The density of the crystals, determined on 5·45 grms. of material, was found to be 4·928 at 15°. They dissolve in water, and the solution deposits crystals of the following salt.

The Salt $5\text{Bi}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$.—If we add water to the mother-liquors from the preceding crystals, we obtain this salt in a well-crystallised form. We do not obtain any other compound than this, no matter what quantity of

water may be added. By mixing 5 litres of water with 2 litres of the mother-liquor of the preceding crystals, I obtained, after eight days, measurable crystals of this salt.

These crystals are not attacked by water, and they do not undergo any change in free air or over sulphuric acid.

The analysis of these crystals, dried in the air until their weight is constant and carried out in the same manner as in the preceding case, gave the following figures:—

	Found.	Calculated for—	
		$5\text{Bi}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$.	$5\text{Bi}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$.
Bi_2O_3	80·05	80·13	79·64
N_2O_5	14·87	14·90	14·81
H_2O (by diff.)	5·08	4·97	5·55
	100·00	100·00	100·00
Calculated for—			
		$6\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$.	
Bi_2O_3		80·30	79·89
N_2O_5		15·55	15·47
H_2O		4·15	4·64
		100·00	100·00

The oxide of bismuth was estimated by the calcination of 6·23 grms. of material air-dried until its weight no longer varied. When dried over sulphuric acid the salt experienced a loss of 0·12 per cent. My colleague, F. Pisani, was kind enough, at my request, to make a control estimation of the nitric acid by Pelouze's method on a sample from another preparation. He found $\text{N}_2\text{O}_5 = 14·76$ per cent.

The composition of the crystals thus approaches closest to the formula $5\text{Bi}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$. For bodies obtained under similar conditions to those which caused the formation of these crystals, the provisional formula $5\text{Bi}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ or $6\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ (or $9\text{H}_2\text{O}$) have been proposed.

The crystals are limpid and brilliant, and take the form of rectangular tables up to 1·6 m.m. in length, 0·3 m.m. in width, and 0·03 m.m. in thickness. They are monoclinic. The faces, β (001) dominant, α^1 (101) and ϵ^1 (011) are observed. Only two faces ϵ^1 (011), are seen. I have measured the following normal angles with the goniometer: β α^1 (001) (101) = 52° 2' and β ϵ^1 (001) (011) = 59° 30'.

On β (001) and α^1 (101) the extinctions are longitudinal. With a strip cut perpendicularly to β (001), extinction takes place at an angle of about 40° with the edge β ϵ^1 (001) (010), in the acute angle β α^1 (001) (101). The plane of the optical axes is in ϵ^1 (010); the elongation is negative.

The density of the crystals, determined with 5·02 grms. of material, was found to be 5·290 at 15°.

Phosphate and Arseniate of Bismuth.

The Salt BiPO_4 .—I have crystallised this body by applying the method which gave me monette, haidingerite, and other crystalline phosphates and arseniates (*Bull. Soc. Chim.*, vol. xxiv., p. 323, vol. xxvi., pp. 18, 24, 81, and 87). I dissolved in a large flask 15 grms. of the salt $\text{Bi}(\text{NO}_3)_3 + 5\text{H}_2\text{O}$ and 7 grms. of the salt $\text{HNa}_2\text{PO}_4 + 12\text{H}_2\text{O}$ in concentrated nitric acid and a little water; I heated the solution on the water-bath, and allowed water to fall into it very slowly drop by drop. After some time the microscopic crystals were collected; they were about 0·15 m.m. long, and 0·05 m.m. thick.

When heated to redness, these crystals suffered no loss. On analysis they gave the following figures, leading to the formula BiPO_4 :—

	Found.	Calculated.
Bi_2O_3 (by diff.)	76·79	76·60
P_2O_5	23·21	23·40
	100·00	100·00

The crystals are limpid and brilliant, and take the form of small monoclinic prisms, elongated along the zone h^1m (100) (110), and terminated by hemipyramids. The face h^1 (100) is often the dominant face. On this face the extinction is longitudinal. The plane of the optical axes is perpendicular to h^1 (100). On m (110) extinction occurs at an angle of about 9° with the elongation in the obtuse angle formed by the edge of the pyramid and of the prism, and the edge h^1m (100) (110). The elongation is negative.

The density of the crystals, determined on 7.55 grms. of material, was found to be 6.323 at 15° .

The Salt BiAsO_4 .—This body can be obtained in the crystalline form if, in the corresponding preparation of the phosphate, we substitute for the disodic phosphate the equivalent amount of disodic arseniate or of arsenic acid.

The crystals are 0.1 m.m. in length and 0.036 m.m. in thickness. They are anhydrous, and analysis gives the following figures leading to the formula BiAsO_4 :—

	Found.	Calculated.
Bi_2O_3	66.80	66.91
As_2O_3 (by diff.)	33.20	33.09
	100.00	100.00

This arseniate is in monoclinic prisms terminated by hemipyramids. They resemble the corresponding phosphate. The face h^1 (100) is wanting. Extinction on m (110) takes place as in the corresponding phosphate. The elongation is negative.

The density of the crystals, determined with 7.80 grms. of material, was found to be 7.142 at 15° .—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 14.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 30TH, 1904.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, February 10th, 1904.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 211 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 211 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford shows a considerable excess for January. The actual amount measured being 3.10 inches, of which 1.3 inches fell on the last two days. The average rainfall for the month is 2.08 inches; so we have an excess of 1.02 inches, equal to 49.0 per cent above the thirty-five years' average.

Our bacteriological examinations of 379 samples taken during last month have given the results recorded in the

following table. Besides these samples we have examined 390 others from special wells, standpipes, &c., making 769 samples in all :—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	310
New River, filtered (mean of 73 samples) ..	16
Thames, unfiltered (mean of 26 samples) ..	8797
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 203 samples) ..	21
Ditto ditto	154
Ditto ditto	0
River Lea, unfiltered (mean of 26 samples) ..	341
River Lea, from the East London Water Company's clear-water wells (mean of 25 samples) ..	14

Of the 301 daily samples taken from the general filter wells of the Metropolitan Water Companies, nineteen samples, or 6.3 per cent, were sterile. Ten samples, or 3.3 per cent, contained more than 100 microbes, and of these, only one sample contained more than 150 microbes per c.c., viz., 154. The ten excess samples contained an average of 119 microbes per c.c. In December thirty-one excess samples contained an average of 156 microbes per c.c. Thus the character of the general supply as regards bacterial impurity has improved greatly during the last month.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

PRECIPITATION AND SEPARATION BY WEAK ORGANIC BASES.*

By E. T. ALLEN.

(Continued from p. 78).

Saponification of Methyl Acetate by N/10 Hydrochloric Acid at 40°C .

25 c.c. acid and 1 c.c. methyl acetate were used in each test. 1 c.c. acid = 0.00374 gm. hydrochloric acid, as determined by sodium carbonate. The process was carried out in sealed tubes as described above :—

a_0 = 1 c.c. of the original mixture in terms of N/20 soda = 2.10.

a_{∞} = 1 c.c. of the mixture when saponification was complete = 9.50.

$a = a_{\infty} - a_0 = 7.4$ = the original mass of methyl acetate in terms of N/20 soda.

Then the saponification constant for a reaction of the first order = $K = \frac{1}{t} \log_e \frac{a}{a-x}$.

Here, of course, t = the time, in this case measured in minutes, and x = quantity of methyl acetate changed, or acid liberated in the time t , again in terms of the soda solution. The Briggs logarithms were used in the calculation.

$t_1 = 131$ m	$x_1 = 2.25$	$K_1 = 0.001204$
$t_2 = 235$ m	$x_2 = 3.55$	$K_2 = 0.001207$
$t_3 = 324$ m	$x_3 = 4.33$	$K_3 = 0.001180$
$t_4 = 363$ m	$x_4 = 4.70$	$K_4 = 0.001206$

Average = 0.00120

Corrected for volume, since 1 c.c. methyl acetate was added to the 25 c.c. acid, $K = 0.00120 \times \frac{26}{25}$.

Corrected for concentration, since the acid was not exactly N/10, $K = 0.00120 \times \frac{26}{25} \times \frac{3645}{3740} = 0.001216 = 1.22 \times 10^{-3}$.

* From the *Journal of the American Chemical Society*, xxv., No. 4.

TABLE V.—Effect of varying the Quantity of Nitric Acid added.

HNO ₃ + Na ₂ HPO ₄ + Molybdate = Na ₂ HPO ₄ + HNO ₃ + Molybdate.					
C.c.	C.c.	C.c.	C.c.	C.c.	C.c.
1	I	4	0.83	2	4
2	I	4	1.04	2	4
3	I	4	1.10	2	4
4	I	4	1.15	2	4
5	I	4	1.24	2	4
6	I	4	0.98	2	4
7	I	4	0.97	2	4
8	I	4	0.88	2	4
10	I	4	0.84	2	4

The intensity of the colour is sharply and regularly affected by the amount of nitric acid present, and it is of particular interest to note that there is a maximum point at which the colour is most intense; with less acid or with more acid present the intensity of colour is considerably reduced, and it is evident that to obtain strictly comparable results the standard and the solution to be read must contain, in a given volume, sensibly the same amount of acid.

Possibly these results are also of interest in throwing light on the precipitation of ammonium phosphomolybdate, and may explain the results sometimes obtained. It is a well-known fact that the colour of the precipitate varies with the amount of acid present from a light lemon-yellow to a deep orange, and the speed with which the precipitate is formed also varies with the amount of nitric acid present. Under the best conditions this precipitation takes place rapidly, and is complete; the supernatant fluid is practically as colourless as water, even when it contains a considerable amount of iron salt. On the other hand, under some other condition the precipitate forms slowly, is "muddy," filters and washes slowly, and shows a decided tendency to run through the filter, while the filtrate generally has a decided colour, due apparently to the ammonium phosphomolybdate still in solution.

The above results show that the presence of 5 c.c. of nitric acid (sp. gr. 1.07) per 50 c.c. of solution gives the most intense colour, and this amount has been adopted for this work. Whether or not this relation gives the optimum condition for the precipitation of ammonium phosphomolybdate, remains to be investigated.

Effect of varying the Quantity of Molybdate.

The effect of varying the quantity of molybdate was studied in the same way. The standard and the solution to be read were identical in all particulars except that in the standard the amount of molybdate present in 50 c.c. was always 4 c.c., while in the other solution the amount of molybdate varied.

TABLE VI.—Effect of varying the Quantity of Molybdate added.

Molybdate + Na ₂ HPO ₄ + HNO ₃ = Na ₂ HPO ₄ + Molybdate + HNO ₃ .					
C.c.	C.c.	C.c.	C.c.	C.c.	C.c.
2	I	5	0.85	4	5
4	I	5	1.00	4	5
6	I	5	1.15	4	5
8	I	5	0.97	4	5
12	I	5	0.96	4	5

The results show considerable differences due to varying the amount of molybdate. These differences are not as great nor is the maximum point as well defined as with different amounts of nitric acid, and there seems to be no reason for changing the amount of molybdate adopted by Woodman and Cayvan as giving the most satisfactory results.

From the foregoing results it appears reasonably certain that in order to obtain reliable and comparable results, the standard and the unknown solution must always contain the same quantities of nitric acid and of molybdate, and be at the same temperature. Should different workers use different amounts of reagent, their results could not be strictly comparable.

Effect of Filter-paper.

In the experiments on the removal of silica, and also in some of those on the loss of phosphoric acid on evaporation of the solution, it was observed that the readings were higher than they should have been. As all the work was done in platinum dishes, the only point where material could get in was where the solutions were filtered to remove silica. In order to determine if anything is taken up from the filter, solutions of various strength were passed through 7 c.m. S. and S. No. 590 paper with the following results:—

Parts per million before filtering.	Parts per million after filtering.	Gain, parts per million.
1	1.16	0.16
1	1.14	0.14
2	2.12	0.12
2	2.17	0.17
5	5.01	0.01
5.5	5.50	0.00

The filters were washed until filtrates had a volume of 50 c.c. each. The results indicate that in passing through the filter these nitric acid solutions of phosphates have taken up silica, phosphoric acid, or organic matter equal to an average reading of 0.15 part per million in four cases, while in two experiments there is no apparent gain. It seems probable that in these latter cases the amount taken up from the paper is masked by incomplete removal of the phosphoric acid from the paper, in the volume of wash-water used. Beyond a doubt filtration introduces a plus error, which may only be apparent in very dilute solutions. Results given in this paper have been corrected in accordance with the above data.

Removal of Silica.

As it is necessary to remove silica from the solution before reading, it was thought that this might be most expeditiously and certainly accomplished by treatment with hydrofluoric acid.

Repeated trials, however, showed that this is not true. While the silica was completely removed finally, it was found that it was necessary to remove all hydrofluoric acid before standardising, as the smallest quantity of fluorides prevented completely the development of the colour. As at least three evaporations with nitric acid were required to accomplish the removal of hydrofluoric acid, the standard procedure of evaporation with nitric acid and drying at 100° for two hours was returned to.

The writer's experience confirms the statement of Woodman and Cayvan, that a single evaporation removes completely the silica from the solution in those cases where lime and magnesium salts are absent, but where lime and magnesium salts are present in considerable quantities, the amount of silica remaining in solution after one evaporation and filtration is too great to be neglected.

For the study of these points a solution of sodium silicate was prepared which, by gravimetric analysis, gave from first evaporation and filtration, 266 parts per million SiO₂; second evaporation and filtration, 2 parts per million SiO₂; third evaporation and filtration, 0 part per million SiO₂; total 268 parts per million SiO₂.

The filtrate from the third evaporation contained no silica by the colorimetric method. 250 c.c. of this silicate solution were transferred and made up to 1 litre, with the view of obtaining a solution containing about as much dissolved silica as is found in many soil extracts.

By calculation from the above determinations this contained 67 parts SiO₂ per million; first evaporation and filtration removed 63 parts SiO₂ per million; second evaporation and filtration removed 2 parts SiO₂ per million; total recovered, 65 parts SiO₂ per million.

By the colorimetric method the solution contained 65 parts SiO₂ per million.

The filtrate from the first evaporation contained, colorimetrically, less than 0.05 part per million, average of four

determinations. The filtrate from the second evaporation contained, colorimetrically, less than 0.1 part per million. The filtrate from the third evaporation contained, colorimetrically, less than 0.1 part per million.

In order to determine the effect of the presence of lime and magnesia salts, a solution containing 25 m.grms. of calcium nitrate and 25 m.grms. of magnesia was added to portions of silicate solution and silica determined colorimetrically as well as gravimetrically.

Gravimetrically obtained:—First evaporation and filtration removed 63 parts SiO₂ per million; second evaporation and filtration removed 5 parts SiO₂ per million; total 68.

Colorimetrically obtained:—67 parts SiO₂ per million; calculated, 67 parts SiO₂ per million.

Filtrate from the first evaporation gave, colorimetrically, 1.42 parts SiO₂ per million. Filtrate from the second evaporation gave, colorimetrically, 0.1 part SiO₂ per million. Filtrate from the third evaporation gave, colorimetrically, less than 0.1 part SiO₂ per million.

From these results it appears that in the absence of lime and magnesia salts the silica left in most soil solutions after one evaporation may be neglected, but in the presence of these salts two evaporations are necessary.

(To be continued).

WHAT PHYSICAL CHEMISTRY HAS DONE FOR CHEMISTRY.*

By HARRY C. JONES.

PHYSICAL chemistry has furnished us with several generalisations which have greatly modified our methods of dealing with chemical phenomena. Among these may be cited the theory of electrolytic dissociation, the law of mass action, Faraday's law, the basis of chemical valence, and the phase rule.

Of these generalisations time will permit us to consider only one or two, and we can only make a few applications of the most important of them all—the theory of electrolytic dissociation.

A word or two in reference to the origin of the theory.

Osmotic Pressure.—When a solution of any substance is brought in contact with the pure solvent, or with a solution of different concentration, at the surface of contact of the two solutions there exists a pressure which tends to drive the dissolved substance from the region of greater to the region of lesser concentration. This is known as osmotic pressure. The first to measure the magnitude of this pressure was the botanist, Wilhelm Pfeffer, who found that salts gave a greater osmotic pressure, for equivalent concentrations, than solutions of substances like cane-sugar.

Origin of the Theory of Electrolytic Dissociation.—It remained for van't Hoff to point out that the electrolytes in general—acids, bases, and salts—exerted a greater osmotic pressure than the non-electrolytes. He also showed that osmotic pressure is a property which depends only upon the number of parts of the dissolved substance in a given volume of the solvent, and not upon the nature of the parts. Since osmotic pressure depends only upon the ratio between the number of parts of the dissolved substance and the number of parts of the solvent, and since electrolytes exert an osmotic pressure that is greater than can be accounted for on the basis of the existence of these substances in the molecular condition, we are forced to the conclusion that the molecules of electrolytes are broken down in solution into parts. These part molecules are called *ions*.

I cannot take up here the evidence bearing upon the theory of electrolytic dissociation, since it would lead much too far. Suffice it to say that the experimental evidence, as far as it has been established in a trustworthy

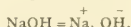
manner, is practically unanimously in favour of the theory, and the amount of such evidence already at hand is simply overwhelming. The theory of electrolytic dissociation is as well established as most of our laws in science, and is to-day almost universally accepted by the leading chemists and physical chemists throughout the world.

Neutralisation of Acids and Bases.—Let us now see what the theory has done for chemistry. Here again we can take up only a few of the many applications of this most important generalisation. Take a class of chemical reactions that are more or less familiar to every one—the neutralisation of acids and bases. It has long been known that when an acid is brought in contact with a base, both are neutralised, and when the solution is evaporated a salt is obtained. Since a different salt was obtained with every acid and base employed, we had as many new phases of the problem of neutralisation as we had acids and bases to react.

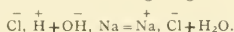
This whole subject has been beautifully unified and simplified by means of our theory. Take the neutralisation of hydrochloric acid with sodium hydroxide. Hydrochloric acid in dilute solution is a mixture of hydrogen ions and chlorine ions:—



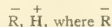
Sodium hydroxide in dilute solution is a mixture of sodium ions and hydroxyl ions:—



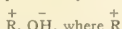
When these solutions are brought together we have:—



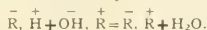
What takes place and all that takes place in the above case is the union of the hydrogen ion of the acid with the hydroxyl ion of the base, forming a molecule of water. The anion of the acid, chlorine, and the cation of the base, sodium, remain after the process of neutralisation in exactly the same condition as before neutralisation took place, and a salt is formed only when the solvent which dissociated the salt into its ions is removed. We may now discuss the subject of neutralisation in general. We may represent any acid by:—



is the anion, which differs in composition for every acid, and the cation hydrogen which is common to every acid. Similarly, we may represent any base by:—



is the cation of the base. Its composition varying with every base, and hydroxyl is the anion common to all bases. When any base reacts with any acid, we have:—



Water is always formed, and the anion of the acid $\bar{\text{R}}$, and the cation of the base $\bar{\text{R}}$, remain in the solution after the process of neutralisation in exactly the same condition as before neutralisation took place. In order to obtain the salt the water which holds the ions apart must be removed.

Neutralisation, then, in terms of our theory consists in the formation of a molecule of water from a molecule of the acid and a molecule of the base, and in nothing else. One process of neutralisation is, therefore, exactly the same as any other process of neutralisation, regardless of the nature of the acid or the nature of the base involved. If this is true it is very important, since it refers all the processes of neutralisation to a common cause—the union of the hydrogen ion of the acid with the hydroxyl ion of the base.

(To be continued).

* From the *Journal of the Franklin Institute*, December, 1903.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, February 4th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. F. G. Smith, H. F. Knight, G. J. Alderton, A. J. Carrier, and F. B. Gatehouse were formally admitted Fellows of the Society.

The PRESIDENT announced that the Council had resolved that a congratulatory address should be sent to Prof. Mendeleeff on the occasion of his 70th birthday on Tuesday, February 9th, a date which would also be that of his official retirement, although he would actually remain at his post for another year.

Certificates were read for the first time in favour of Messrs. Robert Bridgett, M.A., B.Sc., 32, Queen Anne Street, Dunfermline; Tom Sidney Moore, B.A., B.Sc., 99, Rann Street, Birmingham; Clarence Smith, D.Sc., Denmark Lodge, Hatcham, S.E.; Gerald Oscar Morgan-Smith, The Studio, Trowse, Norwich; Reginald Harry H. Stanger, 33, Ladbrooke Grove, W.; John Weinberg, Rosa, United Provinces, India.

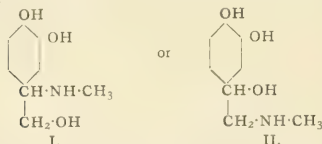
Of the following papers, those marked * were read:—

*16. "The Constitution of Epinephrine." By HOOPER ALBERT DICKINSON JOWETT.

"Epinephrin" was the name given by Abel and Crawford to the active principle of the suprarenal glands, and the substance is identical, when pure, with the "adrenalin" of Takamine and the "suprarenin" of von Furth. As Abel and Crawford were the first to isolate the active principle, although in an impure condition, the author has adopted the name proposed by them. Analysis and molecular weight determinations of carefully purified material confirmed the formula $C_9H_{13}O_3N$, first produced by Aldrich. In dilute acetic acid solution, the compound has $[\alpha]_D - 32.6^\circ$.

On oxidation with potassium permanganate, methylamine and oxalic and formic acids were formed. By fusion with potassium hydroxide, a small amount of a crystalline substance was obtained which gave the protocatechuic acid reaction with ferric chloride. On methylation with methyl iodide and sodium in methyl alcohol and subsequent oxidation with potassium permanganate, trimethylamine and veratric acid were obtained.

The bearing of these results on the constitution of the base was discussed, the following alternative formulae being put forward:—



the second of which was considered the more probable.

*17. "Studies on the Electrolytic Oxidation of Phenols." (Part I.) By ARTHUR GEORGE PERKIN and FREDERICK MOLLWO PERKIN.

When pyrogallol was oxidised in neutral or slightly acid solutions, purpurogallin was precipitated in a very pure condition as an orange-red powder, the best results being obtained with an electrolyte of 15 per cent sodium sulphate. The iridio-platinum anode, which was rotated during the electrolysis, and the leaden cathodes were not separated by means of a porous cell. With a current density of 2 amperes per square decimetre, the E.M.F. was 4.3–4.5 volts (compare *Proc.*, 1903, xix., 58).

When gallic acid was oxidised with an electrolyte of sodium acetate and acetic acid, a black or brown powder was obtained, which was found to be purpurogallin-carboxylic acid. In this case, the current conditions were practically the same as in the preceding experiment, but the anode and cathode were separated by means of a porous cell. The purpurogallin-carboxylic acid thus obtained is not pure, and the yield is very variable.

*18. "Action of Nitrogen Peroxide on 1-Nitrocamphene." By MARTIN ONSLow FORSTER and FRANCES MARY GORE MICKLETHWAIT.

When a current of nitrogen peroxide is passed into a chloroform solution of 1-nitrocamphene (*Trans.*, 1901, lxxix., 644), the temperature rises, crystals separate, and the filtrate becomes bluish-green. The nitrosate, $C_{10}H_{15}O_6N_3$, thus produced to the extent of 24 per cent, is very sparingly soluble in organic media and melts at 217° , when it decomposes; it is probably bimolecular.

The compound, $C_{10}H_{14}O_4N_2$, obtained by the limited action of alcoholic ammonia, piperidine, or potassium hydroxide on the foregoing substance, is insoluble in dilute acids and alkalis; it crystallises from alcohol in prisms melting at 123° , and has $[\alpha]_D - 159.0^\circ$.

By the continued action of alcoholic alkali, a green oil is produced which may also be extracted from the bluish-green chloroform mother liquor of the nitrosate; the substance forms a brown solution in alkali hydroxides, and has not been analysed because it decomposes spontaneously when isolated.

The compound, $C_{10}H_{14}O_5N_2$, formed on oxidising with potassium ferricyanide the green oil dissolved in potassium hydroxide, crystallises from light petroleum in snow-white needles melting at $85-86^\circ$. It dissolves in sodium carbonate and develops a red colouration with ferric chloride; the silver, copper, and ammonium derivatives have been analysed. The bromo-derivative, $C_{10}H_{13}O_5N_2Br$, precipitated when potassium hypobromite acts on solutions in alkali hydroxides, crystallises from alcohol in colourless needles melting at 157° , and has $[\alpha]_D - 68^\circ$. Alcoholic potash regenerates the substance $C_{10}H_{14}O_5N_2$.

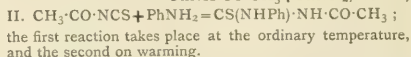
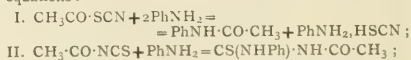
The compound, $C_{10}H_{11}O_5N_2Br_3$, produced by the action of potassium hypobromite on the green oil dissolved in potassium hydroxide, crystallises from light petroleum in pale brown prisms melting at 78° ; it has $[\alpha]_D + 4.2^\circ$.

Methylaminocamphene, $C_{10}H_{15}NHMe$, was prepared by treating with methyl iodide the benzylidene derivative of the primary base, and hydrolysing the product with moist ethyl acetate; it boils at $202-203^\circ$ under 756 mm. pressure, has sp. gr. 0.9171 at 22° , and $[\alpha]_D + 28.7^\circ$ in absolute alcohol. The platinumchloride melts and decomposes at 214° .

19. "The Tautomeric Character of the Acyl Thiocyanates." (A Preliminary Note). By ROBERT ELLIOTT DORAN.

In the course of the present investigation (compare Dixon, *Trans.*, 1901, lxxix., 543), it has been established that the tendency for acetyl thiocyanate either to react as such or to behave as a thiocarbimide, depends almost entirely on the temperature, although the tautomeric change is also influenced to some extent by the nature of the base with which the compound is caused to interact.

Thus, when aniline is employed, it is possible to bring about the changes indicated by either of the following equations:—



the first reaction takes place at the ordinary temperature, and the second on warming.

By means of the latter reaction, several new acetylated thioureas have been prepared, together with others (for example, acetylthiourea), which, although previously described, have not hitherto been obtained directly from the parent substance. The yields obtained with various bases and at different temperatures have also been studied.

20. "Resolution of *α*-Dihydroxybutyric Acid into its Optically Active Constituents." By ROBERT SELBY MORRELL and EDWARD KENNETH HANSON.

Of a series of salts of the active bases with *α*-dihydroxybutyric acid, derived from *α*-crotonic acid, the quinidine salt is the only one which admits of resolution into its two active components, so that these can be separated by crystallisation from water. The quinidine *l*-salt is very sparingly soluble in this solvent, and from it the *l*-*α*-dihydroxybutyric acid has been prepared. The free acid has the same melting point as the racemic substance, but it crystallises in six-sided plates and not in needles. Its specific rotation is 13.5° , this being numerically greater than that of *d*-glyceric acid, which has $[\alpha]_D +2.14^\circ$ (Frankland and Frew, *Trans.*, 1891, lix., 96), and smaller than that of *l*-*β*-hydroxybutyric acid ($[\alpha]_D -24.8^\circ$) (MacKenzie, *Trans.*, 1903, lxxxi., 1402). The barium salts of the *d*- and *l*-acids have been prepared, and the specific rotation of the barium *l*-salt is greater than that of the free acid. Faber and Tollens (*Ber.*, 1899, xxxii., 2598) have described salts of a dihydroxybutyric acid, obtained, together with isosaccharic acid, by the action of lime water on oxycellulose. The rotation of this *α*-dihydroxybutyric acid is given as $+13.7^\circ$, and it is probable that this acid is the *d*-isomeride, corresponding with the *l*-modification obtained from *α*-crotonic acid.

21. "Aromatic Compounds obtained from the Hydroaromatic Series. (Part I.) The Action of Bromine on 3:5 Dichloro-1,4-dimethyl-2,4-dihydrobenzene." By ARTHUR WILLIAM CROSSLEY.

Dichlorodimethylhydrobenzene, on treatment with two molecular proportions of bromine, yields dichlorotribromodimethyltetrahydrobenzene, $C_8H_6Cl_2Br_3$, crystallising in stout, prismatic needles and melting at 118° . When heated to a few degrees above its melting point, this substance rapidly evolves two molecular proportions of hydrogen bromide, giving rise to 3:5-dichloro-4-bromo-*o*-xylene, which crystallises in felted needles melting at 100° . The constitution of this aromatic compound has been definitely decided by synthesis.

If, however, dichlorodimethylhydrobenzene is treated with only one molecular proportion of bromine, an unstable liquid results, which, on heating, loses hydrogen bromide, giving as the main products 3:5-dichloro-*o*-xylene and 3:5-dichloro-6-bromo-*o*-xylene (m. p. 42°).

On further bromination, both these dichlorobromoxylenes give 3:5-dichloro-4:6-dibromo-*o*-xylene, crystallising from ethyl acetate in glistening needles (m. p. 233°), but they differ markedly in their behaviour towards nitric acid.

Thus, 3:5-dichloro-4-bromo-*o*-xylene, on treatment with fuming nitric acid, gives 3:5-dichloro-4-bromo-6-nitro-*o*-xylene, and yields 3:5-dichloro-4-bromo-*o*-phthalic acid when oxidised with dilute nitric acid under pressure, whereas under similar conditions, 3:5-dichloro-6-bromo-*o*-xylene furnishes respectively 3:5-dichloro-4:6-dinitro-*o*-xylene and 3:5-dichloro-6-nitro-*o*-toluic acid.

22. "The action of Nitrogen Sulphide on Organic Substances." (Part I.) By FRANCIS ERNEST FRANCIS and OLIVER CHARLES MINTY DAVIS.

Nitrogen sulphide reacts readily with aromatic aldehydes. Benzaldehyde gives triphenylcyanidin (cyaphenin) and a small quantity of lophin, probably formed by the reduction of the former compound by the sulphur dioxide liberated in the reaction. *p*-Tolualdehyde reacts similarly, giving the corresponding triethylcyanidin. Alisaldehyde, however, yields only very small quantities of *p*-trimethoxyphenylcyanidin, the main product of the reaction being a white, insoluble powder, which is at present under investigation.

23. "Dibenzoylchloroimide." By FREDERICK DANIEL CHATTAWAY.

The author points out that Stieglitz and Earle have overlooked his paper (*Proc.*, 1902, xviii., 165; *Chem. Centr.*, 1902, II., 359), communicated to the Society on June 18th, 1902, which contains a description of the preparation and properties of the diacylchloroimides,

including the dibenzoylchloroimide again described by these investigators (*Amer. Chem. Journ.*, 1903, xxx., 420). Stieglitz and Earle state that, owing to the ease with which the diacylchloroimides are hydrolysed, it is necessary to exclude water entirely in the preparation of these substances. This, however, is contrary to the author's experience, for the chloroimides are readily obtained in the presence of water in the manner indicated in the former paper (*Proc.*, *ibid.*).

Dibenzoylchloroimide, when pure, melts at 86° , or three degrees higher than the temperature given by Stieglitz and Earle.

The diacylchloroimides are readily hydrolysed, yielding the diacylimides and hypochlorous acid either when left in contact with water or when heated with this medium, but the reaction is reversible.

PHYSICAL SOCIETY.

Annual General Meeting, February 12th, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

THE Report of the Council and the Report of the Treasurer were read by the Secretary.

The following Officers and Council were elected for the ensuing year:—

President—R. T. Glazebrook, D.Sc., F.R.S.

Vice-Presidents—Those who have filled the Office of President, together with T. H. Blakesley, M.A.; C. Chree, D.Sc., F.R.S.; Prof. J. D. Everett, D.C.L., F.R.S., and J. Swinburne.

Secretaries—W. Watson, D.Sc., F.R.S., and W. R. Cooper, M.A.

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—Prof. H. L. Callendar, M.A., F.R.S.

Librarian—W. Watson, D.Sc., F.R.S.

Other Members of Council—C. V. Boys, F.R.S.; W. Cassie, M.A.; W. B. Croft, M.A.; H. M. Elder, M.A.; Prof. J. Perry, D.Sc., F.R.S.; A. W. Porter, B.Sc.; W. A. Price, M.A.; Prof. F. T. Trouton, Sc.D., F.R.S.; W. C. D. Whetham, M.A., F.R.S.; S. A. F. White, M.A.

THE PRESIDENT then delivered an Address.

He said that during the last session the attention of the Society had been drawn, by more than one paper, to the study of geometrical optics. He wished now to deal with one or two matters connected with the theory of the microscope. Geometrical optics in its relation to instruments has been studied to great advantage abroad, but, of recent years, has been somewhat neglected in this country. The result is that only a small share in the recent advance in lens construction has been ours. In 1878 Abbe first called attention to the fact that the future perfection of the microscope as an optical instrument depended on the advance of the art of glass-making. With the glasses then at their disposal it was impossible for opticians to get rid of the secondary spectrum of their object-glasses which prevented the attainment of the highest perfection of the image. It was to this fact that the establishment of the firm of Schott and Company was due. Contrasting what is now possible, so far as achromatic correction is concerned, with what was possible say twenty years ago, the President drew attention to the Lick refractor of 56 feet focus, and pointed out that there is a difference of over 3 inches in the positions of the focus for D and H. It would now be possible to construct a lens of 60 feet focus, so that this difference would be reduced to about one-seventh of an inch. Turning to the microscope, and taking Abbe and his pupils as his guide, Dr. Glazebrook analysed the action of the parts of the instrument in order to see if further improvement was possible. It was shown that by the use of two lenses of appreciable focal length, say 100 m.m. each, we can, by placing them at a distance, say 100 m.m. apart, get an equivalent lens of shorter

focus, 1 m.m. in the case in point, and of correspondingly higher power. The advantage of this is obvious; if for no other reason, because of the greater ease of working large lenses. If we imagine a plane perpendicular to the axis of a microscope dividing the object-glass into two parts so that the divergent pencil which falls upon the lens is a parallel pencil when it crosses the plane, we see that a microscope may be considered as a telescope with a short focus lens put in front and used to view an image in the principal focus of that lens. We owe to Abbe the introduction of the term numerical aperture, by which is meant the value of the quantity $\mu \sin \alpha$, where μ is the refractive index of the medium in which the object is placed, and 2α the vertical angle of the cone subtended at the object-glass by the point in which the axis of the instrument meets the object. Let us suppose that an object is on the stage and viewed by transmitted light, and to simplify matters let us suppose the source of light at some distance. Then, according to Abbe and his followers, in considering the image formed in the focal plane of the eyepiece we are not to start from the object as a self-luminous source, and consider where the image of such a source would be if formed by the laws of geometrical optics; we are told to start from the source itself, to consider its image formed in the focal plane of the object-glass, and to treat this image as the source of light in the microscope-tube, from which arises the image we see. If the object be small the focal image will be modified by diffraction by the object; and according to Abbe it is on the nature of the diffraction images and the number of them which are formed, that the definition depends. Suppose the microscope has been focussed on some object on the stage and that this object has been removed; the parallel rays from the source are brought to a focus in the focal plane of the object-glass, forming there a circular patch of light; from each point of this rays diverge and, reaching the eye, produce the sensation of a uniform luminous field. Now let the field in the focal plane be limited by a diaphragm pierced with a series of small apertures. The distribution of light in the focal plane of the eye-lens will be no longer uniform, and we shall see there the diffraction-pattern formed by the apertures. Instead, however, of producing a variable distribution in the focal plane of the object-glass by means of diaphragms, we can do it by means of the diffraction effects of small objects on the stage. Thus, if we put on the stage a grating consisting of a series of equidistant lines, then taking homogeneous light, a series of narrow bands of light, the diffraction images of the source, will be produced in the focal plane with darkness between them. On the assumption that the microscope satisfies the sine condition, the image in the view-plane is the ordinary geometrical image of the grating, a series of uniformly-spaced bright and dark bands. On the distribution of light in the interspaces between the maxima of brightness, the question of resolving power depends. If we modify the number of spectra in the focal plane we modify the image, and this has been done in an ingenious way in some of the experiments arranged by Prof. Abbe's pupils to illustrate his theory. If we cut out all but the central image, the view-field is uniform, no structure is visible; if we allow the first image on either side of the central one to become effective, the bands appear in the field in their proper positions and so on. It is said to be the fundamental result of Abbe's theory that the object (the grating) can be fully resolved if one diffraction image is formed on either side of the central one. It follows from this, that a grating is resolvable if the space between the lines is not less than the result found by dividing the wave-length of light by the numerical aperture. Dr. Glazebrook pointed out that although, by the reasoning he had outlined, the truth of this result could be established, it did not seem to him to prove it. In order to decide whether a grating can be resolved, we must establish the law of variation of intensity in the view-plane, and then consider whether these variations are such that they can be detected by the eye. This has been done by Lord

Rayleigh. The images formed in a microscope are, like all other images, produced by interference; in considering resolving power, we have to consider diffraction effects, it is true, but the diffraction which concerns us mainly is that due to the aperture of the object-glass, and only indirectly to that due to the object viewed. The size of the object on the stage only affects in a secondary manner the method in which the image is formed. It is not necessary, if we know completely the distribution of light over the stage, to go back to the source in a consideration of the problem. Given the distribution over the stage, both in amplitude and phase, we are potentially able to determine that in the view-plane without reference to the source. In the case of a grating illuminated by plane waves, their plane being parallel to that of the grating, we have to consider the effect due to a series of equidistant lines of light. These differ, however, from a series of independent equidistant linear sources, in that the phases of the various sources are the same, and we have therefore to remember that interference will take place between the light from the different lines, while in the latter case there is no relation between the phases, and we can calculate the intensity due to each source separately, and superpose the whole. The method adopted by Lord Rayleigh for the solution of the problem which is presented when a narrow double line in a spectrum is viewed through a telescope, has been applied by him to the microscope (*Phil. Mag.*, Aug., 1896). Dealing with two bright lines and a rectangular aperture, he has shown that, if a variation in intensity of 10 per cent can be detected in the view-plane, then, if the sources are independent, they can be resolved if the distance between them is half that given by Abbe's theory. Lord Rayleigh next considers the effect of a large number of equispaced independent sources, and shows that the view-field has a periodic structure, but that the amount of discontinuity gets less as the sources get nearer together. In the case of a grating with plane-waves incident normally, it is shown that the intensity can be expressed as the sum of a series of periodic terms, each of which corresponds to the effect of two of Abbe's lateral spectra, and that no resolution is possible unless at least the first spectrum on each side is effective. The field in the view-plane corresponds to a series of bright bands at the points corresponding to the geometrical images of the grating; midway between these are a series of less bright bands, while between each pair of these bright bands is an absolutely dark space.

It appears that, while Abbe's theory of microscopic vision is undoubtedly correct in that a small object or objects on the stage produce diffraction patterns in the focal plane of the object-glass, and the illumination in the view-plane can be inferred from these diffraction images, still his method of regarding the question is not the only possible one, neither is it necessary to go back to the original source in order to calculate the illumination. Moreover, we are certain to arrive at erroneous consequences if we apply results obtained from the case of a grating to a case such as that of a small aperture or a small obstacle; the diffraction patterns would be different, and the conditions of resolution different also.

Mr. BECK exhibited a series of microscopes in which diffraction-gratings on the stages were viewed with different arrangements of slits placed in the focal planes of the object-glasses, which illustrated the various points of Abbe's theory.

Preparation of Primary Alcohols by means of the Corresponding Amides.—L. Bouveault and G. Blanc. —The authors obtain, by means of sodium ethylic alcohol and the caproic, pelargonic, and phenylacetic amides, the corresponding alcohols:—(1) Normal hexylic alcohol, $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$, boiling at 156° ; (2) normal nonylic alcohol, $\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{OH}$, boiling at 215° ; (3) phenylethyl alcohol, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$, boiling at $212-215^\circ$. These examples show that this reaction is general, —*Comptes Rendus*, cxxxviii., No. 3.

NOTICES OF BOOKS

The Manuring of Market Garden Crops. By BERNARD DYER, D.Sc., F.I.C., and F. W. E. SHRIVELL, F.L.S. Reprinted from the *Journal of the Royal Horticultural Society*, Vol. xxviii., Part 4. London: Vinton and Co., Ltd. 1903. Pp. 120.

The experiments carried out by the authors have now reached their tenth year. This pamphlet contains the records of the first eight years, and, to a partial extent, those of the ninth year.

The work done resolves itself very largely into an enquiry as to whether or not the large quantities of purchased dung now used by the market gardeners are being used to the greatest economical advantage.

It is well known that market garden crops are manured more heavily than almost any others, and most of the manures used are chiefly nitrogenous, and the market gardener is too often not aware that by neglecting to supply the phosphates necessary to balance the nitrogen in them, he is preventing them from doing their full work.

The experiments which have been carried out at the Hallow Experimental Station, Golden Green, indicate over and over again that heavy dunging for most crops is wasteful and unprofitable, and that a much lighter dressing of dung, supplemented by chemical fertilisers, is the best application. The experiments cover all kinds of market garden produce, and the pamphlet is fully illustrated with photographs showing the different yields obtained from dung alone, and dung with chemical fertilisers, or the latter alone.

An Elementary Text-book of Metallurgy. By A. HUMBOLDT SEXTON, F.I.C., F.C.S., &c. Third Edition, thoroughly Revised and Enlarged. With numerous Illustrations. London: Charles Griffin and Co., Ltd. 1903. Pp. 263.

The first edition of this text-book was published in 1894; it has evidently been well received, as we have now before us the third edition. This addition has been revised, and though the scope and plan of the book have been unchanged, there have been a few additions and many minor alterations.

Beginning as it does with the nature of metallurgy and the properties of metals, this book is specially adapted for the use of students. By its study they will acquire a good grounding in the science, and will the more easily understand the special methods and processes they intend to follow in the future.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

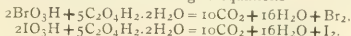
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxviii., No. 3, January 18, 1904.

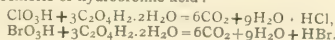
Zinc Peroxides.—M. de Forcrand.—The author makes a series of experiments on the peroxides of zinc. He proves the existence of a compound $\text{ZnO}_{1.75} + \text{H}_2\text{O}$ or $\text{Zn}_4\text{O}_7 + 4\text{H}_2\text{O}$, which corresponds to one limit; then a very unstable compound $\text{ZnO}_{1.98} + 2$ or $2.5\text{H}_2\text{O}$; the degree of oxidation of this compound approaches very near to ZnO_2 . Finally, by the action of heat on these former substances he isolates $\text{ZnO}_{1.66} + \text{H}_2\text{O}$ or $\text{Zn}_3\text{O}_5 + 3\text{H}_2\text{O}$, and $\text{ZnO}_{1.66} + 0.66\text{H}_2\text{O}$ or $\text{Zn}_3\text{O}_5 + 2\text{H}_2\text{O}$. At 190° and 210° respectively these two compounds suddenly decompose, giving an almost anhydrous protoxide without intermediate products.

Method of Separation of Aluminium and Iron by the Use of Formic Acid.—A. Leclère.—The author succeeds in separating aluminium and iron very exactly by the precipitation of the aluminium in the form of basic formate. For example, using a dilute solution containing a slight excess of sulphuric acid, first the iron is reduced to a protoxide salt. For this purpose it is best to use ammonium hyposulphite, as no residue is left in the precipitates. Ammonium formate is then added, and the whole kept boiling. The iron is kept in the form of protoxide, whilst the aluminium is precipitated gradually, not in the state of sulphite, but of basic formate mixed with a little sulphur. When drying the precipitate nitric acid should be added to drive off the formic acid and to prevent the presence of a residue of carbon in the calcined alumina. The iron can be precipitated by the addition of sulphuretted hydrogen to the liquid filtrate. The sulphide is produced.

Estimation of Chlorates, Bromates, and Iodates.—Léon Debourdeaux.—The estimation of chloric, bromic, and iodic acids can be made by determining the proportion of the halogen which is contained in the compound after it has been transformed by calcination into the alkaline or argentic chloride, bromide, or iodide. This estimation can be effected by a volumetric method analogous to that used for the estimation of nitrates, and founded on the following facts:—1. Oxalic acid is not destroyed at boiling-point by a solution containing less than 20 c.c. of concentrated sulphuric acid per 100 c.c. 2. Oxalic acid in a liquid containing 12 c.c. of concentrated sulphuric acid per 100 c.c. is destroyed by chloric acid according to equation $\text{ClO}_3\text{H} + 2\text{C}_2\text{H}_4\text{H}_2 \cdot 2\text{H}_2\text{O} = 4\text{CO}_2 + 6\text{H}_2\text{O} + \text{ClOH}$, and by bromic and iodic acid according to equations—



However, in the absence of an intermediate oxidation these reactions are not quantitative. 3. Oxalic acid in a solution containing 5 grms. of manganese sulphate and 12 c.c. of strong sulphuric acid per 100 c.c. is destroyed in a regular manner by chloric and bromic acid, with formation of hydrochloric or hydrobromic acid:—



Iodic acid acts as in the case mentioned in (2), only the yield is theoretical.

New Method of Synthesis of Tertiary Alcohols by means of Organomagnesium Compounds.—V. Grignard.—The author starts with a compound of the form $\text{RC} \equiv \text{OMgX}$, obtained as he has described in a former paper, and by performing on the second oxygen atom, a reaction identical with that on the first, he should obtain the complex $\text{R}' > \text{C} \begin{smallmatrix} \text{OMgX} \\ \text{OMgX} \end{smallmatrix}$, the hydrolysis of which would give the ketone $\text{R.CO.R}'$. He finds, however, a scarcely appreciable quantity of the ketone formed, but instead a very good yield of the tertiary alcohol, RC(OH):R_2 .

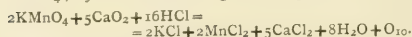
MISCELLANEOUS.

Royal Institution.—On Tuesday next, February 23, Mr. E. Foxwell, late Professor of Economics and Finance at the Imperial University, Tokyo, will deliver the first of three lectures at the Royal Institution, at 5 o'clock, on "Japanese Life and Character"; and on Thursday (February 25), at the same hour, Prof. H. L. Callendar will commence a course of three lectures on "Electrical Methods of Measuring Temperature." The Friday Evening Discourse, on February 26, will be delivered by Mr. Alexander Siemens, his subject being "New Developments

in Electric Railways"; on March 4, by Prof. W. Stirling, on "Breathing in Living Things"; and on March 11, by Prof. F. T. Trouton, on the "Motion of Viscous Substances."

Speed of the Reaction between Permanganate of Potassium and Oxalic Acid.—R. Ehrmfeld.—In the absence of sulphuric acid the solutions of permanganate and of oxalic acid decomposed according to the equation $8C_2H_2O_4 + 2MnO_4K = 2C_2O_4Mn + C_2O_4K_2 + 10CO_2 + 8H_2O$. The reaction takes place rapidly at 50–60°. Towards the end of the reaction the liquor takes a reddish-yellow colour, and finally becomes cloudy; on boiling it forms brownish flakes on the surface. The author has examined the speed of the reaction at 20.3° by estimating at various times the amount of undecomposed permanganate by means of a solution of KI. The reaction between the permanganate and oxalic acid is a unimolecular reaction; in all cases the products formed by the reaction determine an increase in the speed of the reaction. This speed depends also on the concentration of the solutions, which shows that a portion of the undecomposed permanganate enters into the reaction.—*Zeit. Anorg. Chem.*, vol. xxxiii., p. 117.

Iodometry of the Peroxides of Calcium, Strontium, Barium, Magnesium, and Sodium.—E. Rupp.—The titration of the peroxides of the alkalis and the alkaline earths can be effected by the method described by the author for the estimation of the persulphates and the percarbonates. With all these oxides the general reaction is as follows: $—MO_2 + 4HCl + 2KI = MCl_2 + 2KCl + 2H_2O + I_2$. The iodine set free is estimated with hyposulphite of soda. As for checking the results obtained by this method, this can easily be done by estimating the same oxides by $KMnO_4$; by this means CaO_2 gives the equation—



When used simultaneously, both methods constantly give concordant results.—*Arch. d. Pharm.*, vol. cxl., p. 437.

MEETINGS FOR THE WEEK.

- MONDAY, 22nd.—Society of Arts, 8. (Cantor Lectures). "Modern Book Printing," by Charles T. Jacoby.
Society of Chemical Industry, 8. "Duty-free Alcohol," by Thomas T. Iyer.
- TUESDAY, 23rd.—Royal Institution, 5. "Japanese Life and Character," by Ernest Foxwell, M.A.
- WEDNESDAY, 24th.—Society of Arts, 8. "Mahogany and other Fancy Woods available for constructive and Decorative Purposes," by Frank Tiffany.
- THURSDAY, 25th.—Royal Institution, 5. "Electrical Methods of Measuring Temperature," by Prof. H. L. Callendar, F.R.S.
- FRIDAY, 26th.—Royal Institution, 6. "New Developments in Electric Railways," by Alexander Siemens, M. Inst. C. E.
Physical, 8 (At Royal College of Science, South Kensington). "A New Dynamometer," by Mr. Bormisen.
"A Quartz-thread Vertical Force Magnetograph," and "Some Hints on the Preparation of Diagrams," by Dr. W. Watson. "On Sir-uses in a Magneto-static Field," by G. W. Walker.
- SATURDAY, 27th.—Royal Institution, 3. "The Life and Work of Stokes," by Right Hon. Lord Rayleigh, F.R.S.

THE ROYAL WATERLOO HOSPITAL FOR CHILDREN & WOMEN,
WATERLOO BRIDGE ROAD, S.E.

There is a vacancy for a fully qualified HEAD DISPENSER at the above Institution. Applications can only be entertained from those in possession of the Pharmaceutical Society's qualifications.

Particulars may be obtained from the SECRETARY at the Hospital, to whom applications, with testimonials, &c., must be forwarded on or before FEBRUARY 23rd.

BIRKBECK COLLEGE

(BIRKBECK INSTITUTION),

Breams Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board, Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.

INSTRUCTION IN

PURE CULTIVATION OF YEAST. According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts brewers', distillers', wine, disease yeasts, moulds, and bacteria.

Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jørgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

The Laboratory supplies for direct use: Cultures of yeast for brewers, distillers, wine manufacturers, &c.

Further particulars on application to the Director—
ALFRED JØRGENSEN, The Laboratory, Copenhagen, V.

A. C. COSSOR,

Original Maker of "X" RAY TUBES in England.

FOCUS TUBES giving finest possible definition. IMPROVED TUBE HOLDERS, with arrangement for securing wires to avoid perforation of tube.

All kinds of "X" Ray Apparatus. Mercury Pumps, Screens, Spill Gaps, &c. Applications for Price Lists invited.

Glass Blowing.

All kinds of Experimental Glass Blowing carried out for Scientific Men, Laboratories, &c.

INVENTORS' IDEAS WORKED OUT AS PER INSTRUCTIONS.

COSSOR,
54, FARRINGTON ROAD, E.C.



Hittori's Tube showing the resistance of the dark space.

MARTINDALE'S Apparatus and Reagents For Chemical and Bacteriological Research.

SPECIALITIES:—

MARTINDALE'S BURETTE STAND 9/-, 15/-

MARTINDALE'S BACTERIOLOGICAL CASE 42/-

Analytical Price List post free. Telephone—1797 Paddington.

W. MARTINDALE, 10, New Cavendish St., W.

ABSOLUTE ALCOHOL,

FREE FROM DUTY,

FOR SCIENTIFIC AND RESEARCH WORK IN LABORATORIES.

To be obtained from

HUGO LORENZ,

7-8, Idol Lane, Great Tower St., London, E.C.,

Licensed Trader in Alcohol and Spirits of Wine.

Stock kept in suitable packages ready for immediate use.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2309.

CONTRIBUTIONS TO OUR KNOWLEDGE OF RADIUM.

By W. MARCKWALD

I. ON THE SEPARATION OF RADIUM FROM BARIUM.

HITHERTO only one method has been available for the separation of a mixture of salts, richer in radium, from the radium-barium salts as obtained from the uranium minerals. By the fractional crystallisation of the chlorides (according to Curie) or, more advantageously, of the bromides (according to Giesel) it is possible to accumulate the radium salt to any desired extent in the more difficultly soluble fractions. This method of crystallisation is very detailed, because of the isomorphism of the barium and radium salts (*cf.* W. Marckwald, *CHEMICAL NEWS*, 1901, lxxxiv., 190; Rinne, *Centralbl. f. Min. u. Geol.*, 1903, 134—141).

The idea that it might be possible to separate the two alkali earths from one another, by a suitable electrolytic method, induced me to arrange an experiment the result of which confirmed this conjecture. The concentrated aqueous solution of a quantity of radium-barium chloride* was allowed to stand, and shaken up frequently with about a fifth of its weight of sodium amalgam. Only a very slight decomposition of water takes place, but a very considerable part of the sodium goes into solution as ion, while an equivalent quantity of radium and barium amalgam is formed. The proportion of radium to barium in the amalgam is by no means the same as in the solution, but is very much higher. If the amalgam is separated from the solution after the action has lasted one to two hours, decomposed with hydrochloric acid, and the small quantity of chloride resulting on the evaporation of the hydrochloric acid solution is compared on the phosphorescence screen with an equal quantity of the salt remaining in the original solution, then it appears, without any necessity for applying a more delicate method of measuring, that the first salt far exceeds the latter in activity.

By repeating the operation many times, after first properly neutralising the solution, we obtain from the amalgams fractions of salts, the activity of which gradually decreases.

In the above form, the new method of accumulating the radium offers no important practical advantages over the crystallisation method, for in both cases the aim in view is only reached by a process of fractionation. Whether it is possible to simplify the process for obtaining radium from the raw product by further development of this method does not yet appear. Meanwhile, this observation which I now communicate is of interest, because for the first time a difference is exhibited in the behaviour of radium and barium.

II. ON THE PHOSPHORESCENCE OF THE ANHYDROUS RADIUM BARIUM CHLORIDE.

It is well known that mixtures of anhydrous radium and barium chloride, even when they contain very little active salt, are strongly phosphorescent, while the hydrous crystalline salts either do not phosphoresce at all or only very slightly. This phenomenon is to be ascribed to the fact that phosphorescence is excited in anhydrous barium chloride by the Becquerel rays, both by α - and β -rays, and

not in the hydrous crystalline salt. Thus, if a little rod coated with radio-tellurium, which only emits α -rays, is brought up to the first salt, it becomes brightly luminous, as well as at the approach of a radium preparation enclosed in an aluminium capsule, which gives out only β -rays. On the other hand, the crystalline hydrous barium chloride shows no phosphorescence under the same conditions.

III. ON INDUCED RADIO-ACTIVITY.

The interesting publication of F. v. Lerch (*Ann. d. Phys.*, [4], xii., 745) on the induced thorium activity leads me to communicate some observations on the induction of the radio-activity of radium solutions on metals, although the research is not yet completed.

Freshly prepared solutions of radium salts, which had been kept in a dry state for a long time, and had thus reached their maximum activity, are, according to Curie's and Giesel's researches, strongly active, but the activity rapidly dies away—according to Rutherford because the emanation is given up—until it has reached a minimum. If in the solution of the radium barium chloride mixture, as it is obtained directly from the Joachimsthal pitch-blende, metals are immersed after the solution has stood for many days, these are rendered only very feebly active by induction, but if freshly prepared solutions are used, after remaining a short time in the solution certain metals become very strongly active. This activity reaches its maximum in from 15 to 30 minutes, and slowly diminishes in the course of a day after removal from the solution. The induced metal emits both α - and β -rays, which in the case of some metals are strong enough to enable the phosphorescence of the zinc blende screen by direct radiation (α -radiation), as well as that of the barium platinum cyanide screen, through a layer of cardboard (β -radiation) to be seen even in an imperfectly darkened room. A noteworthy difference is shown between the different metals as regards the intensity of the induction. Under exactly the same conditions, the degree of induced activity appears to depend generally on the position the metals occupy when arranged in a series, according to their contact forces. At any rate the induction decreases in the metals magnesium, zinc, tin, copper, silver, bismuth, palladium, in this order, and the differences are so great that in observing the action on the phosphorescence screen it is at the most only in the case of neighbouring members of the series that there can be any doubt.

If many strips of the same metal are immersed in the same solution of the salt one after another at short intervals, *i.e.*, after about one to two hours, generally no noticeable diminution of the inductive action is to be observed. An exception must be made only in the case of magnesium. While the first strip becomes very strongly active, all the subsequent ones are only feebly acted upon. This phenomenon must be ascribed to the fact that the solution, by the immersion of the first magnesium strip, becomes alkaline, if only to a very slight extent. This is inferred chiefly from the fact that magnesium is made very strongly active, and the action is continuous, if the solution is kept acid by the addition of a small quantity of hydrochloric acid.

It might be thought that in acid solution the surface of the metal is kept clean, while in neutral solution it is covered with a layer of oxide, and that this hinders induction. Hence a little ammonium chloride was added to the neutral solution of the radium salt; thus the magnesium oxide was dissolved, the solution becoming alkaline. In this case the strong inductive action was absent.

These observations led me to examine the behaviour of zinc and copper in a solution of radium chloride made feebly alkaline by ammonia, and in another made feebly acid by hydrochloric acid. It then appeared that the zinc, which is chemically allied to magnesium, behaved in an exactly analogous manner, while the copper was about equally strongly acted upon in both solutions.

In conclusion, it must be mentioned that all these experi-

* For this experiment a mixture of salts was used, which had been obtained from Joachimsthal pitch-blende without further increasing the proportion of radium.

ments were confined to the feebly active radium preparation mentioned above. Whether radium salts containing high percentages will give analogous phenomena has not yet been examined.—*Berichte der Deutsch. Chem. Gesell.*

THE INVARIABILITY OF THE WAVE-LENGTHS IN THE SPARK AND ARC SPECTRUM OF ZINC.

By J. M. EDER and E. VALENTA.

THE breadth of the lines in the arc and spark spectrum is a complicated, and as yet only partially known function of the temperature, pressure, and the density of the luminous layer of vapour (H. Kayser*), and is probably dependent on the kind of electric excitation, and of the dielectric (Hartmann†). The experimental observations of these phenomena of broadening are as yet by no means finally concluded. In particular it is not yet known whether the intensity maximum—in a certain measure the centre of gravity of a spectral line—is displaced when it broadens or not, which is a question of fundamental importance for the whole of spectrum analysis.

Actual displacements of spectral lines (i.e., clearly demonstrable alterations of the wave-lengths) have undoubtedly been proved by Humphrey and Mohler‡ as a consequence of variable external pressure.

But F. Exner and E. Haschek went distinctly further when they said that these displacements occurred with greater intensity in the spark spectrum than in the arc, and depended not only upon the external atmospheric pressure but also on the partial density of the vapour under examination (Exner and Haschek, "Wellenlängen Tabellen für Spektralanalytische Untersuchungen," Leipzig und Wien, 1902, p. 13). They further stated that many spark spectra show considerable displacements of the spark lines as opposed to the analogous lines in the arc spectrum (in both cases at ordinary external atmospheric pressure), and tried to explain this by the pressure phenomena in the spark (These *Sitzungsber.*, 1897, *et seq.*), and would calculate from the magnitude of the displacements of the lines the magnitude of the pressure in the spark; E. Haschek and H. Mache (These *Sitzungsber.*, 1898) tried to demonstrate the pressure in the spark directly, but could obtain no agreement of the values calculated from the "displacement of the lines" with the observed values. From his further researches, E. Haschek (These *Sitzungsber.*, Bd. cx., Abt. II.a, März, 1901, p. 181) afterwards concluded that the laws which hold good for the displacements of the lines in the spark are different from those which obtain in the case of the arc, and that therefore a calculation of the spark pressure from the displacement of the lines is not admissible; the spark pressure observed from Haschek's measurement showed so little agreement with that calculated by him that he himself said:—"The calculated pressures differ so much among themselves that there can be no doubt that other causes are responsible for the displacements of the lines" (Haschek, *loc. cit.*). As such another cause of the "line displacements" Haschek mentions "the increasing density of the luminous vapour"; with equal increase of the vapour density it is said that "the lines in the spark spectrum are displaced more than those in the arc spectrum"; thus, for

example, according to Haschek, in the zinc spectrum the lines $\lambda 3282$, 3302 , 4680 , 4722 have in the spark spectrum a wave-length greater by 0.03 to 0.16 Angström units than in the arc; in other cases Haschek mentions displacements up to 0.2 A.U. for elements with many lines, and up to 0.07 A.U. for elements with few lines, which are very considerable amounts, lying far beyond the limits of errors of observation permissible with grating spectra. As a proof of the correctness of these observations he performed numerous wave-length measurements (with different elements, e.g., B, Al, Zn, Ca, Si, Zr, Cr, Ti, Ce, Va, &c.). From these statements it seemed as if the existence of real line displacements was certainly proved for the spark (as opposed to the arc lines) for ordinary external atmospheric pressure. Also the quantity of the vaporising substance, according to Haschek, is said to have an appreciable influence on the actual wave-length of the lines, so that in his opinion a method of quantitative spectrum analysis could be based on the measurement of these so-called line displacements (These *Sitzungsber.*, Bd. cx., Abt. II.a, February, 1902, p. 232). For example, for pure zinc (spark spectrum) the wave-length 4722.510 is said to be correct, while it amounts only to 4722.399 for the same zinc line, using a 5 per cent zinc alloy instead of pure zinc as electrode. Thus the partial density in the luminous vapour would have a definite influence on the wave-length.

The theory relating to the dependence of the wave-length of the spectral lines on the partial density of the vapour under examination occupies a prominent position in the work by F. Exner and G. Haschek, "Wellenlängentabellen für Spektralanalytische Untersuchungen auf Grund der Ultra-violetten Funkspektren der Elemente" (Leipzig und Wien, 1902, I. Teil, p. 13). The comprehensive numerical results which the above authors give as obtained in their wave-length measurements would force us to acknowledge the value of this evidence in their favour, if we could suppress our well-grounded doubt concerning the value of the evidence afforded by their photographic material.

On an earlier occasion we had already obtained results which did not agree with their statements in the case of the spark spectra of calcium and lithium, as we pointed out at the time (we drew attention to the fact that photographic errors might have occurred), and when we began new wave-length measurements in the zinc spectrum we again met with experimental results which were contradictory to Haschek's statements. Also our results with regard to the spectra of alloys both poorer and richer in zinc do not agree with Haschek's statements and measurements.

H. Kayser, of Bonn ("Handbuch der Spektroskopie," Bd. ii., pp. 297, 308, 309, and 310), also opposed Exner and Haschek's statements; he stated that during his spectroscopic researches on the electric arc he had never observed any influence exerted by the mass of the element present on the wave-length, and according to his view the partial pressure of the vapour in the arc could produce no displacements, as can be easily proved if we work with apparatus of considerable resolving force, while otherwise apparent displacements may result. As regards the comparison of the wave-length in the spark with the arc lines, and the influence of the partial pressure on displacements of the lines in the spark spectrum, at present no further experimental confirmation exists regarding Exner and Haschek's assumption of displacements of the lines.

It may here be stated explicitly that it is not a question of the breadth of the lines in the so-called asymmetrical phenomenon of broadening, which has been known for many years, and which amongst other things manifests itself in

* "Handbuch der Spektroskopie," Leipzig, 1902, Bd. II., p. 296.

† *Sitzungsber. der Königl. Preussischen Akad. der Wiss.*, Berlin, 1903, p. 40, and 234.

‡ *Astrophys. Journ.*, 1896 and 1897. Humphrey and Mohler increased the pressure of the gas, in which the arc is produced, to several atmospheres, and observed the displacement of some spectral lines towards the red, and they found that the increase of wave-length is proportional to the pressure of the surrounding gas.

§ No notice at all is taken in this treatise of displacements of lines caused by rapid movement of the sources of light in the radius of vision in the sense of Doppler's principle, which displacements are proved for the measurement of the movement of the stars in the radius of vision.

* Meanwhile, N. A. Kent has proved that in the case of the titanium lines Haschek's displacements of 0.13 A.U. do not exist (*Astrophys. Journ.*, 1903, Bd. xvii., p. 286).

† Eder and Valenta, "Über das Funkspektrum des Calciums und Lithiums und Seine Verbreiterungen und Umkehrerscheinungen," *Denkschr. Akad. der Wiss. Wien.*, 1898, Bd. lxvii.

such a way that with pure metal electrodes (e.g., zinc, lead, &c.) spectral lines in the spark from a jar are decidedly broadened towards the red, and, on the other hand, the same lines become fairly well defined if these metals in the electrodes occur only as small impurities (thus with small partial density) in the vapour. In the case of Exner and Haschek's phenomenon of the displacement of the lines, it is a question rather of the exact wave-length of the intensity maximum of the lines* which, in a certain measure, represents the "centre of gravity" of the lines concerned.

If we take as basis for such measurements the intensity maximum of the lines in question, which is now recognised both generally and also by Haschek (*These Sitzungsber.*, 1902, Bd. iii., Abt. II.a, p. 232) as the only permissible method of taking such measurements with correct photographic procedure, and the most accurate possible resolution of the spectra, we arrive at results which contradict Haschek's statements.

We first attacked the zinc spectrum and devoted ourselves exclusively for a long time to eight zinc lines, which could be taken as typical, and which, in addition to other similar spectra, were brought forward by Haschek as affording specially valuable evidence in favour of his theory.

Our grating is an excellent large Rowland's concave grating with a radius of curvature of 15 English feet (i.e., the same radius of curvature as that of the grating used by Exner and Haschek), which H. Kayser, of Bonn, who saw our spectrum photographs, calls a grating "of the very first order." Now, with asymmetrically broadened lines—and Haschek's research only applies to such—the possibility of finding the intensity maximum with certainty depends on restricting the broadened extended part by the most careful photographic procedure. We worked with a slit of 0.008 to 0.03 m.m. breadth (sharp steel knife edges), which last even gave good definition of the lines, ascertained the true photographic focus of the grating by empirically removing† the photographic plates 1 m.m. at a time, and bent the photographic mirror plates focally with the curvature of the image. We arranged the photographing of the lines one over the other in such a way that a blind for the slit, which could be easily removed to and fro, could be interposed before the photographic apparatus, and by moving this blind every line could be photographed in three parts one after the other. At each separate operation the whole grating was fully illuminated. The illumination of the plate was short.

No agreement has yet been arrived at regarding the idea of a "short illumination" or "minimum illumination" with the best clearness and sharpness and correct development. As long as this is the case, differences of observations with regard to the so-called displacement phenomena of spectral lines, as E. Haschek repeatedly describes them, in contradiction to other spectroscopists, will exist, and it will be difficult to avoid deception. In order to fix definitely the sharpness of the lines, the breadth of the measured line should not only be expressed in Angström units (A.U.), but the "degree of blackening" of the line in question on the photographic negative should also be given; the latter should be fairly small. It may be regarded as a criterion whether a photograph will meet the strictest requirements if an asymmetrically broadened line is obtained with medium or least blackening with a certain minimum breadth. We measured the breadth of the sharp iron lines resulting under favourable experimental conditions in the arc spectrum; they were, for example, 0.03 to 0.04 m.m. broad with a slit of 0.03 m.m. breadth (with minimum illumination) when they produced, measured in Hartmann's microphotometer a blackening of 0.5 to 1.0; while the zinc

lines, when strongly subjected to the broadening under exactly the same conditions, were never narrower than 0.06 m.m. in the negative of the spectrum. If the scale is reduced to A.U. the zinc line $\lambda 4810$ has thus in the arc a breadth of 0.07 A.U. against 0.19 A.U. in the spark (in both cases with minimum illumination); nevertheless, we can easily prove the coincidence of the two lines at the position of their greatest light intensity. But if we illuminate the zinc spark twice as long, the asymmetrical broadening is so marked that the total breadth of the line amounts to 0.53 to 0.71 A.U., and then it is difficult to find the maximum of the light intensity; the central part of the line is shifted towards the red; but it is still possible to think that the maximum has been reached, and thus an apparent displacement of 0.008 A.U. may be found, which increases to 0.02 A.U., and with long illumination, bad development, and imperfect reading in consequence of feeble light, can amount to still more. The reason for this apparent displacement is to be found in the fact that the central part of the line is not more resolved. Also the placing has an appreciable influence. When it is not perfectly exact, asymmetrically broadened lines become unrecognisable and disappear.

It is difficult to decide whether this is sufficient to explain the very contradictory statements of different spectroscopists who have photographed one and the same phenomenon, but it is a fact that by carefully carrying out the spectrographic process as described, we succeeded in proving the non-existence of all alleged displacement phenomena, which Haschek described for zinc, as well as for other spectra.

The arrangement of our experiments, as regards the production of the spark discharges in question between zinc electrodes, exactly agreed with those experimental conditions under which Haschek thought he had proved the existence of "line displacements." In his "Spektralanalytische Studien" (*These Sitzungsber.*, 1901, Bd. cx., Abt. II.a., p. 200) he says expressly that the lines were displaced more with the Ruhmkorff inductor and hammer interruption, than when a similar inductor with Wehnelt interruption, or when a transformer was used. Hence, we also used powerful Ruhmkorff induction coils with hammer interruptors; we had two large inductors, striking at a distance of 12 to 25 cm., with correspondingly large condensers, so that a real displacement phenomenon could not possibly have escaped us.

But under these conditions the asymmetrical broadening phenomena of the zinc lines $\lambda 4680, 4722, 4810, \&c.$, appeared clearly, and in our experiments we obtained at once one of the phenomena which Exner and Haschek call displacement phenomena. Fig. 1. of our heliographic table shows two zinc spectra* accurately photographed one above the other, which immediately make it clear how the "displacement phenomenon" appears. As a matter of fact, from a superficial inspection one would be inclined to pronounce in favour of a displacement of the lines, although a displacement of the true intensity maximum does not actually occur. Similar false "displacement phenomena" also appear under other different experimental conditions; if the photographs of the zinc lines are illuminated too long they present this appearance, if we produce them on the one hand with pure zinc electrodes, and on the other with zinc alloys, which only contain a little zinc, which is interpreted by Exner and Haschek as the influence of the partial pressure of the vapour; also with defective definition of the spectra, the zinc lines taken for the sake of comparison in the arc (narrow lines) and in the spark (asymmetrically broadened) generally look similar. But it may at once be stated that the two spectra in Fig. 1. were obtained from one and the same zinc spark, with short and long exposure (one-half minute to five minutes),† and that the supposed displacement of lines is only the photographic expression of the asymmetrical broadening, as the photograph of a wedge-shaped, outlined

* Specially discussed and illustrated by us in our treatise "Funkenspektrum des Calciums und Lithiums und Seine Verbreitungen und Umkehrerscheinungen" (*Wiener Zeit. Deutsch.* 1903).

† In such spectrum photographs, in which the highest definition is required, a change of 1 m.m. in the plane of position (with a total focus of 6 m.) produces very considerable disturbances.

* Facsimile of the original negative in heliogravure.

† N.B.—The finer lines in Spectrum 2 are iron lines photographed in.

streak of light would show it with lengthened exposure, even if the intensity maxima had remained quite constant. The spectra, when very shortly illuminated, give only the intensity maximum of the lines which coincide, while with longer illumination the line of the spark spectrum broadens more towards the red than towards the side of shorter wave-length, and with rather longer development of the photographic plate the intensity maximum of the line is united with the asymmetrical broadening. After the conditions under which the phenomenon in question appears are explained, we can pass to the description of the results of our own experiments in which those circumstances liable to give rise to error were carefully avoided. When every precaution is taken to ensure minimum illumination, the plates are correctly developed and the spectra best defined, it appears:—

1. That at ordinary atmospheric pressure there occur no displacements, which are said to appear, according to Exner and Haschek, in the spark spectrum as opposed to the arc spectrum.

2. That also in the spark spectrum no displacements of the lines exist, which were to be ascribed to small quantities of the element present in the vapour, *i.e.*, that any dependence on the partial pressure in the sense of Exner and Haschek's assumptions cannot be proved.

In both cases only the known variable asymmetrical broadenings of the lines occur, but the brightness maxima of the lines coincided perfectly in our experiments.

We studied the same zinc lines in which Haschek observed displacements in the spark spectrum, and first determined their wave-length as accurately as was practicable, using Rowland's standard, corrected by Kayser ("Normale aus dem Bogenspektrum des Eisens," *Ann. der Physik. und Chemie.*, 1900, 4 Folge, Bd. iii., p. 195); the lines were measured under the microscope, each line at least ten times on different spectrum photographs, so that our wave-length observations are correct to 0.002 Å.U.

As according to Haschek the lines in the arc spectrum of zinc show the normal wave-length, and with small partial pressure, in Haschek's sense, are better for ascertaining the normal wave-length (without any fear of the disturbing so-called "displacement phenomena"), we chose for the formation of the zinc arc spectrum, brass wire (in the small electric arc),* which according to chemical analysis contained 36.9 per cent zinc and 63.1 per cent copper.

The carefully determined wave-lengths of the zinc lines of such an arc light between brass electrodes gave for the arc spectrum:—

Zinc—III. order		λ 3302.715
" " "		3303.068
" " "		3345.141
" " "		3345.698
" " "		3282.451
" II. " "		4680.327
" " "		4722.333
" " "		4810.719

In the same field of vision in the arc spectrum, next to them came the copper lines of the third order, λ 3247.671 and 3274.090 (Rowland) which in the arc appear reversed (symmetrically broadened), while the arc spectrum of iron, photographed as normal, contains a trace of copper and gave a fine black copper line, which coincided perfectly with the phenomenon of inversion.†

Our heliographic table, Fig. II., 1 and 2, shows the exact spectrum photograph of the arc spectrum of a zinc-copper alloy; it is clear how with increasing illumination all the lines of the arc spectrum remain fairly sharp, and broaden symmetrically. Pure zinc gives in the spark

spectrum λ 4680, 4722, 4810, with increasing illumination asymmetrically broadened strongly towards the red, but with exact minimum illumination, the brightest part of the line appears sharp enough in the strongest spark from a jar to fix exactly its wave length, and to be able to establish under the microscope its coincidence with the arc line, which is evident from our table (Fig. II., 1—4). With the zinc lines λ 3282, 3302, 3345.1, we found likewise perfect coincidence in the arc lines and spark lines; the zinc spark lines λ 3345.1 and 3302.7 are easily reversed, and then coincide perfectly with the (unreversed) arc line. With over-illumination a broadening of this line towards the ultra-violet occurs. The zinc line 3345.698, which is to be obtained well-defined and clear, both in spark and arc, without difficulty, and 3303.068 are considered by Haschek himself as not capable of displacement, because their tendency to remain well-defined even with inexact times of illumination prevents any error which could exist with defective definition in the case of the zinc lines 4680, 4722, &c., which broaden asymmetrically.

Fig. III. shows in Spectrum 1 and 3 the spark spectrum of pure zinc; Spectrum 2 in the middle is the arc spectrum of the zinc-copper alloy, and over all three is extended the arc spectrum of an iron wire containing traces of copper. We see the perfect coincidence of the reversed copper arc line λ 3247, and 3274 with the unreversed copper spark line. The zinc lines, λ 4722 and 4810 (Fig. III.), are rather much illuminated and developed to strong blackness, by which means the arc lines of the middle spectrum have broadened on both sides fairly uniformly, while the spark lines show asymmetrical broadening and the beginning of apparent displacements, which disappears with minimum illumination and shorter development, after which the perfect coincidence analogous to Fig. II. becomes undoubtedly evident.

In the zinc lines, λ 3345 and 3302 of Fig. III., we further see that these zinc lines in the spark, as compared with the arc lines, are by no means displaced towards the side of greater wave-length, as Haschek (*loc. cit.*) erroneously states. We see this still more clearly in the measurement of the original negative under the microscope of the measuring apparatus.

The supposition that Haschek had badly-defined spectra gains in probability owing to the fact that the finer structure of some zinc spark lines, which is very remarkable, escaped him. While the asymmetrical very marked broadening of the zinc lines 4680, 4722, 4810 towards the red did not escape Haschek, he did not notice that the zinc lines λ 3345.1 and 3302.7 show a tendency to slight broadening towards the side of shorter wave-length, and hence they lose the tendency to apparent "displacements" towards the red. Nevertheless, Haschek finds the lines in the spark specially strongly displaced towards the red (as compared with the arc), and we find, on the contrary, that here with correct short exposure generally no displacement, but coincidence, results.

After we had failed to establish the results quoted as relating to the line displacements in the spark as opposed to the same lines in the arc, there still remained further experiments to be arranged on the influence of the partial pressure of the luminous zinc vapour on the displacement of the spectral lines. For this purpose we subjected to an accurate investigation the spark spectrum of pure zinc and that of alloys of 1 per cent zinc + 99 per cent lead, as well as 50 per cent zinc + 50 per cent lead and 36.9 per cent zinc and 63.1 per cent copper. In the case of alloys poor in zinc, according to the experience of all spectroscopists, which was first published long ago and is now generally known and never disputed—and this holds good for all spectra, especially with asymmetrically broadened lines—all those lines, even with increasing illumination, remain fairly sharp, which, in alloys rich in zinc, undoubtedly show in a high degree the tendency to asymmetrical broadening. Thus far the partial pressure undoubtedly exerts an influence on the breadth of the spectral line.

* The brass electrodes were used directly for the production of the arc.

† In agreement with these experiments of ours, Exner and Haschek in their "Wellenlängentabellen," Bd. 1, p. 21, speak of the two copper lines 3247 and 3274 as not capable of being displaced.

Thus, with increasing time of illumination, the asymmetrical broadening phenomena in the case of alloys rich and poor in zinc are not the same; thus, if we measure on the more strongly illuminated plates the wave-length of alloys rich and poor in zinc by placing on the middle of the badly-defined lines, apparent line displacements appear with rising partial pressure (analogous to the photograph in Fig. 1.), which, however, we at once recognise as apparent displacements if we have returned to minimum times of illumination and have obtained the best defined spectra.

A 1 per cent zinc alloy (1 per cent zinc + 99 per cent lead) naturally gives the separate zinc lines in the spark less clearly than one richer in zinc, e.g., a 50 per cent zinc alloy. A preliminary test for our strongest spark (Ruhmkorff) showed that the poorer alloy (1 per cent) must be illuminated for about fifteen minutes, as compared with about thirty seconds for the richer (50 per cent) in order to get the zinc lines 4680, 4722, 4810 approximately equally sharp (equally bright) on the photographic plate for both alloys. Hence in our preliminary experiment in the first case the zinc lines would be thirty times brighter than in the second.

If, now, we use equivalent times of illumination and approach the minimum time of illumination, which in both cases gives faint, just measurable lines in the spectrogram, in the spark spectrum the wave-lengths of the zinc lines 4680·327, 4722·333, and 4810·719 in 1 per cent, 4 per cent, and 50 per cent alloys, and in pure zinc, are exactly the same, and we could never—even with the strongest jar spark—see Exner and Mache or Haschek's "line displacements."

Haschek (These *Sitzungsber.*, Feb., 1902, Bd. cxi., Abt. II.a, pp. 238 and 240) states that alloys with a little zinc (4 per cent zinc) give in the spark spectrum zinc lines of wave-lengths λ 4722·399, but with 50 per cent zinc this becomes 4722·434, which would be a considerable displacement towards the red with increasing partial pressure; he finds the zinc line 4680 in alloys poor in zinc (4 per cent zinc) too faint to be measured. But this line 4680, even in 1 per cent alloys, can be measured (this is shown clearly in our table, Fig. IV., 4) if we choose the time of illumination properly. Haschek has obviously under-exposed the alloy poor in zinc and over-exposed the richer alloy, and was deceived by an asymmetrical broadening of the lines with defective definition of his spectra. As far as we can see, Haschek applies his theory of displacement only to asymmetrically broadened lines; with the sharp lines not even the apparent displacement of the lines is to be seen in the spark spectrum as opposed to the arc spectrum.

Thus our results are:—

1. In the spark spectrum of zinc, as opposed to the arc spectrum, no displacements of measurable magnitude appear.

2. The mass of the element present, or the partial pressure of its vapour, produces no displacement of the lines of the spark spectrum, and hence Haschek's system of quantitative spectral analysis falls to the ground; on the contrary, those conclusions which presuppose the constancy of the spectral lines (displacements of the spectral lines in the radius of vision according to Doppler's principle, &c.), and which appeared doubtful owing to Haschek's deductions, are further confirmed by our observations.—*Sitzungsber. der Kaiserl. Akad. der Wiss. in Wien.*, Bd. cxii., Abt. II.a, October, 1903.

Formation and Saccharification of Retrograde Amidon.—L. Maquenne.—The author concludes that amyocellulose is not a single principle, but a mixture of several different products of condensation which have the common characteristic of not being coloured by iodine. It has also the distinctive characteristic of offering a variable resistance to the solvent action of amylase.—*Comptes Rendus*, cxxxviii., No. 4.

ON THE COLORIMETRIC DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID AND OF SILICA.*

By F. P. VEITCH.

(Concluded from p. 91).

The Colorimetric Determination of Silica.

In their study of the effect of silica on the development of colour, Woodman and Cayvan (*Journ. Am. Chem. Soc.*, xxiii., 96) found that while some colour was developed instantly, it did not reach the maximum intensity in less than from one and one-half to two and one-half hours, and their results further show that the colour due to the formation of the ammonium silico-molybdate is about one-tenth that produced by an equivalent amount of ammonium phosphomolybdate. This reaction apparently was used first by Jolles and Neurath (*Zeit. Angew. Chem.*, 1898, p. 315) for the determination of silica in waters. For our determination of silica a solution of sodium silicate was prepared and the silica determined gravimetrically. Portions of this solution were compared with the standard phosphate solution under identical conditions as to temperature, nitric acid, molybdate solution, and volume. The data obtained are given in the following table:—

TABLE VII.—Readings of SiO₂ in Terms of P₂O₅.

SiO ₂ in solution read. M.grms.	P ₂ O ₅ required to equal colour produced by SiO ₂ . M.grms.	1 m grm. SiO ₂ equals P ₂ O ₅ . M.grms.
<i>Preliminary Series.</i>		
0·10	0·19	1·90
0·10	0·175	1·75
0·20	0·35	1·75
0·20	0·37	1·85
0·30	0·51	1·70
0·30	0·57	1·90
0·50	0·92	1·84
0·51	0·90	1·78
0·70	1·35	1·93
0·70	1·28	1·83
1·00	1·80	1·80
Average		1·82
<i>Final Series.</i>		
0·068	0·1265	1·86
0·136	0·2464	1·81
0·204	0·3741	1·83
0·272	0·4785	1·78
0·340	0·5907	1·73
Average		1·80

The table shows that the intensity of colour produced by the silica is on an average 1·8 times that produced by an equivalent amount of phosphoric acid. That is, the phosphate readings divided by 1·8 or multiplied by 0·55 equals SiO₂.† It will be seen from the final results, in which most reliance is placed—as they were obtained after considerable experience with the method—that there is a gradual decrease in this factor with increasing quantities of silica. The time required for the full development of the colour was much shorter than found by Woodman and Cayvan, apparently reaching the maximum in less than twenty minutes, after which time it remained stationary for some time, and then slowly faded.

On the basis of this work the procedure which I have adopted for the determination of silica and phosphoric acid in soil solutions is as follows:—

The water or extract is tested for iron by adding potassium ferrocyanide to the acidified solution. The absence

* From the *Journal of the American Chemical Society*, xxv., No. 2.

† These results differ greatly from those given by Woodman and Cayvan, but so far no time has been available for further study of this point.

of interfering amounts of iron having been shown, a measured volume of the water or soil extract is freed from suspended matter by filtration or by passing through a Chamberland filter (reject the first 100 c.c. that passes), or by evaporating to dryness and filtration, or in some cases where the water is but slightly turbid the turbidity or colour is corrected for by determining its amount in terms of the standard, the reading thus obtained being afterwards subtracted from the final readings. Add to the clear extract 5 c.c. of nitric acid (sp. gr. 1.07) and 4 c.c. of molybdate solution. Place in the camera, allow ten to thirty minutes for development of colour, and compare with a standard phosphate solution, which may conveniently contain 10 parts per million of phosphorus pentoxide and be contained in a sliding tube connected by rubber tubing with a side neck tube graduated in cubic centimetres within the camera. (The colour of the standard is not affected by the rubber tube during one working day, but the standard should be made fresh each day). The readings thus obtained (several should be made and the average taken) minus the reading for turbidity, when calculated to a volume of 100 c.c., equals P_2O_5 ; SiO_2 in parts per million of solution.

Another measured portion of the water or extract is evaporated to dryness twice, with a filtration between the evaporations in a porcelain or platinum dish with 3 c.c. nitric acid (sp. gr. 1.07) plus a little magnesium nitrate,* heated two hours in a water-oven, 5 c.c. nitric acid (sp. gr. 1.07) added, filtered, washed to about 45 c.c., placed in a camera, and compared. If coloured, the reading is noted, and is finally subtracted from the total reading. Add 4 c.c. of ammonium molybdate, and thoroughly mix. Place in the camera, and compare after two to five minutes. The corrected reading calculated to volume of 100 c.c. is P_2O_5 in parts per million of solution. This reading subtracted from the $SiO_2 + P_2O_5$ reading and the difference multiplied by 0.55 gives the silica.

Where the original solution is too much coloured with organic matter to be accurately corrected for by reading the colour thus produced against the standard phosphate solution, it is necessary to evaporate with about 0.1 gm. magnesium nitrate* and burn off the organic matter, take up with water + 3 nitric acid, evaporate to dryness, and heat two hours in the water-oven. Add 5 c.c. nitric acid and proceed as above. Readings = P_2O_5 . In this case silica is not determined.†

In pure solutions the method gives very close readings and very accurate results on dilute solutions. The average error has been well within 0.2 part per million of the solution read where these solutions did not contain more than 10 parts per million and the readings fall below 60 scale divisions on the colorimeter tube. This insignificant error of reading may give rise to larger differences when calculated on the basis of the dry soil. Should the solution to be examined contain more than 10 parts per million, its dilution to this strength and subsequent calculation to the basis of the original solution or to the dry soil may so multiply this error of reading as to render the results valueless. This has been a serious handicap to the method. The use of more concentrated solutions is obviously the rational way out of the difficulty. It is also obvious that here we are limited to the use of concentrations from which the phosphomolybdate will not precipitate, within an hour or so. As solutions of greater concentration than 10 parts per million cannot be read closely in 25 m.m. tubes, with ordinary light, and as larger tubes were not available, I have not tried greater concentrations in larger tubes, but in several experiments using a strong standard (between 50 and 100 parts per million), in shallow depths in the 25 m.m. tubes, it was not found possible to read closer than

The results given in the following table have been obtained in the course of the work:—

TABLE VIII.—Determination of $SiO_2 + P_2O_5$ in Miscellaneous Samples.

	Parts per million.			
	SiO_2 present.	SiO_2 found.	P_2O_5 present.	P_2O_5 found.
Sodium phosphate solution, No. 1	—	—	49.6	48.5
Sodium phosphate solution, No. 2	—	—	99.1	101.4
Sodium silicate solution ..	182.0	180.5	—	—
Soil extract—No. 13.. ..	—	24.4	—	2.0
" 14.. ..	—	23.4	—	2.95
" 15.. ..	—	21.2	—	2.95
" 16.. ..	—	19.1	—	2.95
1st foot.. ..	—	17.9	—	7.3
2nd	—	8.2	—	1.0
3rd	—	7.8	—	3.1
4th	—	11.9	—	1.4
Soil No. 2806, sandy truck soil	—	2.0	—	10.0
Soil No. 2795, loam soil ..	—	38.0	—	8.0
Soil No. 3, clay soil ..	—	30.0	—	8.0
Soil No. 2804 clay soil ..	—	28.0	3 grav.	4.0
Sodium phosphate solution—				
Original solution (readings made for Prof. F. K. King)	—	—	—	73.1
First 50 c.c. through Chamberland filter.. ..	—	—	—	59.1
Second 50 c.c. "	—	—	—	67.6
Third 50 c.c. "	—	—	—	71.8
Left in 50 c.c. in "	—	—	—	80.3
Rinsings of "	—	—	—	80.3
Original solution	—	—	—	80.25
First 50 c.c. through Chamberland filter.. ..	—	—	—	54.9
Second 50 c.c. "	—	—	—	71.8
Third 50 c.c. "	—	—	—	84.5
Left in 50 c.c. in "	—	—	—	97.2
Rinsings of "	—	—	—	84.5

from 0.5 to 1 part per million. This error of reading, when calculated back to the original solution or to the dry soils, gives as great an error as the closer readings of the more dilute solutions, so this line of study was not carried further.

In addition to this study conducted with known solutions, the method has also been applied to the soil samples sent out this year by the Association of Official Agricultural Chemists. The results thus obtained are given in the following table, with results obtained by the standard methods for determining phosphoric acid. The average total reading in scale divisions and the corrections on each sample, also in scale divisions, are given in the table. These corrections are for original colour of the liquid and for filter-paper.

TABLE IX.—Phosphoric Acid Soluble in Distilled Water. Parts per Million of Dry Soil. 400 c.c. of Solution used for the Determinations.

No.	Average total scale readings.	Correction in scale readings.	Reading due to P_2O_5 .	P_2O_5 volumetric.	P_2O_5 volumetric.
2	13.5	1.5	12.0	1.50	1.33
3	10.0	1.5	8.5	1.06	0.64
4	10.0	1.5	7.5	0.94	1.26
5	10.0	3.0	7.0	0.87	0.99
6	48.5	5.5	42.0	5.60	5.10
7	23.0	2.5	20.5	2.56	2.63
8	20.0	3.0	17.0	2.12	1.95

The results given are all that the writer has obtained on soils. No determinations have been rejected.

Precautions.

The method is so delicate (one scale division means one-half of one part per million on basis of dry soil when the

* In solutions containing sufficient base to form normal phosphates with all the phosphoric acid, the addition of magnesium nitrate appears to be unnecessary.

† Or the organic matter may be destroyed by treating with aqua regia in the presence of sufficient base to prevent loss of phosphoric acid.

solution is prepared by treating 1 part of soil with 5 parts of water and taking 50 c.c. for the determination), and as has been shown there are so many points at which errors may be introduced, that a final word as to the precautions to be observed in handling it may be given with propriety.

The sodium phosphate ($\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$) from which the standard is made must be practically pure and be free from silica and iron. It is convenient to make a solution containing 100 parts phosphorus pentoxide per litre, and then dilute this to 10 parts per litre for the reading standard. The greatest care should be used in making this standard, as it is here where errors count. Ten c.c. of the 100 parts per litre solution should be run into a standardised 100 c.c. flask from an accurately graduated burette. Make up to a volume at $20-25^\circ \text{C}$. with distilled water (free from $\text{SiO}_2 + \text{P}_2\text{O}_5$), add 10 c.c. of nitric acid (1.07) and 8 c.c. of ammonium molybdate, and mix thoroughly. This is the standard with which the unknown solutions are to be compared, and it should be made fresh each day.

All reagents, including distilled water, must be kept in Jena glass-ware, tested from time to time, and made fresh when a mixture of them shows colour after standing some time.

As the colorimetric tubes may have a slight colour themselves, each should be tested, and its reading carefully established. This may be done by filling the tubes with distilled water and reading them with a 1 part per million standard.

The standard and the unknown solution must contain, in equal volumes, equal amounts of reagents, and be at sensibly the same temperature.

The solution must contain less than 20 parts per million of iron (Fe).

A correction must be established for each package of filter-paper used. This correction is small, but not to be neglected on S. and S. No. 590 paper.

When the solution contains much lime or magnesia it is best to make two evaporations and filtrations before comparing.

Observing all precautions and making all corrections there is a maximum error of ± 2 scale divisions (each scale division = 1 c.c.) in the reading. When the soil solution is made by treating 1 part of soil with 5 parts of water, and 50 c.c. are taken for the determination, the error on the dry soil is ± 2 parts per million; when 100 c.c. are taken for the determination the error is ± 1 part per million, so that the working errors may only be neglected when at least 200 c.c. of solution are taken for the determination.

PRECIPITATION AND SEPARATION BY WEAK ORGANIC BASES.*

By E. T. ALLEN.

(Concluded from p. 89).

Saponification of Methyl Acetate by Phenylhydrazine Hydrochloride at 40°C .

COMPARING the following results with those for aniline hydrochloride, we note that there is an acceleration in the rate of saponification in both cases. With aniline hydrochloride, this is comparatively small; with the phenylhydrazine compound, considerable. If the periods of time had been successive instead of overlapping, the acceleration would be seen to be actually greater than the figures indicate. If we compare the values for a , we have $a = \text{N}/10$ hydrochloric acid, 7.4; $\text{N}/10$ aniline salt, 7.49; $\text{N}/10$ phenylhydrazine salt, 9.12.

$a_0 = 1.78$	$a_{\infty} = 10.90$	$a = 9.12$
$t_1 = 1330$	$x_1 = 0.37$	
$t_2 = 2419$	$x_2 = 0.57$	
$t_3 = 4290$	$x_3 = 1.55$	
$t_4 = 5683$	$x_4 = 2.33$	
$t_5 = 6960$	$x_5 = 3.02$	

$$K = 1.67 \times 10^{-3} \times \frac{26}{25} = 1.73 \times 10^{-3} \div 1.22 \times 10^{-3} = 1.4 \text{ p. c.}$$

$$K = 1.44 \times 10^{-3} \times \frac{26}{25} = 1.50 \times 10^{-3} \div 1.22 \times 10^{-3} = 1.2 \text{ p. c.}$$

$$K = 2.38 \times 10^{-3} \times \frac{26}{25} = 2.47 \times 10^{-3} \div 1.22 \times 10^{-3} = 2.0 \text{ p. c.}$$

$$K = 2.89 \times 10^{-3} \times \frac{26}{25} = 3.00 \times 10^{-3} \div 1.22 \times 10^{-3} = 2.5 \text{ p. c.}$$

$$K = 3.27 \times 10^{-3} \times \frac{26}{25} = 3.40 \times 10^{-3} \div 1.22 \times 10^{-3} = 2.8 \text{ p. c.}$$

This means that, by some secondary reaction, more acid has been formed than the methyl acetate could furnish. On this account it seems more rational to calculate the percentages hydrolysed from the earlier periods of the process. This leads us to the approximate values 1.5 per cent for the phenylhydrazine salt and 2.0 per cent for the aniline compound. Many other experiments on the saponification of methyl acetate were made with other preparations of the salts, but since all led to the same conclusions, and the table given above contains the results obtained under the most carefully regulated conditions, no others have been quoted.

In calculating the values of $K = \frac{1}{t} \log_e \frac{a}{a-x}$ for the phenylhydrazine salt, a was taken equal to 7.4.

A similar case of acceleration in the saponification of methyl acetate was noticed by Ley (*Zeit. Phys. Chem.*, xxx., 231) when he employed solutions of aluminum and lanthanum chlorides.

He attributed the acceleration to a secondary action between the chloride and acetic acid, setting free the more highly dissociated hydrochloric acid.

If we compare aniline and phenylhydrazine in regard to their power to precipitate the weak inorganic bases, it appears that their strength is nearly the same, but that of aniline is slightly less. (See Table F).

The precipitations were all made in the cold, with solutions containing about 1 m.-gm. of metallic oxide per cubic centimetre, and all were slightly acid. 15 c.c. of each solution and about 1 c.c. of the reagent, a large excess, were taken for each test. Where any difference is found in the behaviour of the two bases, it is seen that phenylhydrazine precipitates more rapidly; and in one instance, beryllium sulphate, it precipitates where aniline has no action. That both reagents bring down the same precipitates one can scarcely doubt. They all closely resemble the hydroxides (or basic salts) formed by ammonia, being flocculent and white, or nearly so, when the reagents are free from colour and the solutions are dilute. The colour of phenylhydrazine is partly borne down by the precipitates. I have noticed that solutions containing free nitric acid in some quantity form yellow or brown products, which are probably oxidation products, and which colour the precipitates. The addition products which are formed by the action of the same bases on the chlorides of zinc, cadmium, and mercury, and by phenylhydrazine on the chlorides of cobalt and nickel as well, are entirely different in appearance; in fact, they are crystalline.

Regarding the difference in the behaviour of the nitrates and sulphates of the same elements, too little has been done to draw conclusions, but it will be noticed that where any difference exists, the sulphates precipitate more rapidly. The chlorides have not been systematically compared with the sulphates, but enough has been done to show that they behave similarly to the nitrates, in precipitating less rapidly and sometimes less completely than the sulphates. This may be due to the formation of basic salts in the case of the sulphates, precipitates which possess a different solubility from the hydroxides, or perhaps the sulphates of the organic bases are less dissociated than the chlorides.

TABLE F.

Salt.	Action of aniline.	Action of phenylhydrazine.
Be(NO ₃) ₂ ..	Trace of precipitate	Same as with aniline.
BeSO ₄ ..	No precipitate	Heavy precipitate, though not complete.
Al(NO ₃) ₃ ..	Precipitation slow, but complete	Complete and much more rapid precipitation.
Al ₂ (SO ₄) ₃ ..	Complete precipitation	Complete precipitation.
Cr(NO ₃) ₃ ..	Complete, but slow precipitation	Complete and rapid precipitation.
Cr ₂ (SO ₄) ₃ ..	Complete precipitation	Complete precipitation.
Ti(NO ₃) ₄ ..	" " " "	" "
Ti(SO ₄) ₂ ..	" " " "	" "
Zr(NO ₃) ₄ ..	Precipitation complete, but slow	Precipitation complete, and considerably more rapid than with aniline.
r(SO ₄) ₂ ..	Complete precipitation	Complete precipitation.

Concentration of Free Acid in the Solutions Precipitated by Organic Bases.

The solutions in which the previously described separations were made are too complicated in composition to deal with directly. All contained an unmeasured quantity of ammonium salt, while some contained also several different acids. A few experiments were therefore carried out under simplified conditions.

Experiment 1.—100 c.c. titanium sulphate containing 0.0944 gm. titanium dioxide were precipitated with ammonia, and the washed precipitate was transferred by a jet of water to an empty beaker. A measured quantity of hydrochloric acid, greater than that theoretically demanded, was then introduced. After warming and stirring, a large part of the precipitate remaining undissolved, an excess of phenylhydrazine was poured in. The precipitate was then filtered, while the filtrate was carefully tested for traces of titanium. None was found. It is evident that we have here data which, with the value of the hydrolytic constant of phenylhydrazine hydrochloride will enable us to calculate the quantity of free acid present. For if m equals the number of molecules of the phenylhydrazine salt, l equals the number of molecules of excess of base, v equals the volume of the solution in litres, k equals the hydrolytic constant, and a equals the degree of dissociation,—

$$k = \frac{a(m+l)}{v(1-a)} \text{ and } a = -\frac{kv+l}{2m} + \sqrt{\frac{kv}{m} + \left(\frac{kv+l}{2m}\right)^2}.$$

Total weight of acid = 0.238.

Phenylhydrazine required = $0.238 \times \frac{108}{36.5} = 0.704$ gm.

= 0.006521 gm.-molecule.

Phenylhydrazine used = 1 c.c. = 1.09 gm.

Phenylhydrazine in excess = $1.09 - 0.704 = 0.386$ gm.
= 0.003575 gm.-molecule.

$m = 0.006521$ Hence $a = 0.001$, i.e., we have 0.006521
 $l = 0.003575 \times 0.001 \times 36.5 = 0.2$ m.-gm. of free
 $v = 0.00002$ acid in 100 c.c.
 $v = 0.2$ litre.

Experiment 2.—In this experiment all the conditions were the same as in Experiment 1, except that only 0.8 c.c. phenylhydrazine was used.

$m = 0.006521$ Hence $a = 0.0027$, i.e., we have 0.60 m.-gm. of
 $l = 0.001555$ acid in 200 c.c.
 $v = 0.00002$
 $v = 0.2$ litre.

Experiment 3.—To a quantity of freshly precipitated and washed alumina equivalent to 0.1257 gm. Al₂O₃, was added a very slight excess of hydrochloric acid, viz., 0.280 gm.; all the precipitate dissolved. At a boiling temperature, 2 c.c. phenylhydrazine gave a practically complete precipitation, but the precipitate was very slimy, and the conditions were not adapted to practical work. The excess of phenylhydrazine here is quite large, but other experiments with a smaller excess failed to precipitate the alumina completely.

Here $m = 0.007672$ gm.-molecule.
 $l = 0.01251$ gm.-molecule.
 $v = 0.00002$
 $v = 0.1$

Hence $a = 0.00008$ and the free acid = $0.007672 \times 0.00008 \times 36.5 = 0.02$ milligram. per 100 c.c.

The concentrations of free acid in the above cases were probably a little larger than those in the solutions with which the practical work was done, for in the latter cases there was an ammonium salt which must have tended to reduce dissociation.

It is quite certain that titanium hydroxide can be quantitatively precipitated in solutions more strongly acid, but we have here, no doubt, about the same amount of free acid as in the practical work.

There is some reason to believe that the calculated values given above are somewhat too small, for I found that blue litmus-paper, while it was decidedly reddened by the solutions we have just considered, gave hardly any reaction with solutions prepared by adding the calculated amount of free acid to 100 c.c. distilled water.*

I am unable to explain this discrepancy. Possibly the value 2×10^{-8} for the hydrolytic constant of phenylhydrazine hydrochloride is too small, though one would be inclined to suspect that the method used would give high rather than low results. At all events it appears probable, in view of all the facts, that the concentration of free acid in the solutions we have been considering is not greater than a few milligrams. in 100 c.c.

Summary.

1. The weak organic bases, such as show little or no alkaline reaction with indicators, on account of the hydrolysis of their salts, can, of course, never completely neutralise the acid of a metallic salt. They therefore cannot precipitate the strong metallic bases, but only the weak ones, which are practically insoluble in very dilute acid. The precipitate may be either the hydroxide or a basic salt. All the analytical separations with these weak bases, which have been devised thus far, seem to involve this principle. The strong reducing power of phenylhydrazine gives it a particular advantage in certain cases.

2. The work described in this paper was done with phenylhydrazine and aniline. These two bases are of about the same strength, aniline being slightly weaker. This conclusion was arrived at by the study of the saponification of methyl acetate by their hydrochlorides, and also by their power to precipitate metallic hydroxides. The saponification constants in N/10 solutions at 40° C. were found to be 2.5×10^{-8} for the aniline salt, and 1.7×10^{-8} for the phenylhydrazine salt. These numbers lead us to the values 4×10^{-8} and 2×10^{-8} , respectively, for the hydrolytic constants. This means that about 2 per cent of the former and 1.50 per cent of the latter are decomposed into free base and free acid, under the conditions of dilution and temperature stated above.

3. The concentration of free acid in solutions from which the metallic hydroxides were separated must be quite small. The calculated values amounted to but a few tenths of a milligram. for such volumes as 100 to 200 c.c. There is some reason to think these values are too small, but it is not likely that they reach above a few milligrams. in the above volumes.

4. Aniline quantitatively precipitates the quadrivalent

* A sensitive litmus tincture, however, reacted strongly with these solutions.

and weakly basic elements, titanium, zirconium, cerium, and thorium, as well as the trivalent elements Fe^{+++} , Al , and Cr^{+++} under certain conditions, from dilute and slightly acid solutions. The solutions may be chlorides, nitrates, or sulphates. The same statements apply to phenylhydrazine, except that ceric and ferric salts are reduced by this reagent to salts of comparatively strong bases which are precipitated incompletely or not at all.

Zinc, cadmium, mercury, cobalt, and nickel, when sufficiently concentrated, form difficultly soluble addition products with phenylhydrazine. With aniline, also zinc, cadmium, and mercury give similar compounds. The strongly basic elements, magnesium, barium, calcium, strontium, manganese, and ferrous iron are not precipitated (*Journ. Am. Chem. Soc.*, xxi., 779).

Beryllium, when present alone, is not precipitated by aniline, nor by phenylhydrazine, except from sulphate solutions. Actual separations were worked out as follows:—Titanium and zirconium from iron; titanium, zirconium, and thorium from beryllium. The separation of aluminum from iron proposed by Campbell and Hess was studied more closely. A double precipitation is advisable in all these separations. The separations from ferrous iron depend upon the reducing power of phenylhydrazine as well as its weakly basic nature. Aniline cannot be substituted for it here, but all the separations from beryllium may be done equally well with aniline.

5. Phenylhydrazine will accurately separate minute quantities of alumina (and probably also the weaker bases) from large masses of iron.

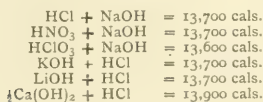
WHAT PHYSICAL CHEMISTRY HAS DONE FOR CHEMISTRY.*

By HARRY C. JONES.

(Concluded from p. 91).

Heat of Neutralisation.—We have a means of testing this crucially by experiment. If the process of neutralisation is independent of the nature of the acid and the nature of the base, the amount of heat set free when any completely dissociated acid acts on any completely dissociated base in equivalent quantities, will be a constant.

The fact is that a constant amount of heat (13,700 cal.) is liberated when a gram.-equivalent weight of any completely dissociated acid is brought in contact with a gram.-equivalent weight of a completely dissociated base. A few examples will make this clear:—



If we vary the nature of the acid or the nature of the base, the amount of heat set free is a constant to within the limit of experimental error. Fact and theory are thus in perfect accord.

Thermoneutrality of Salts.—Another application of the theory of electrolytic dissociation in thermochemistry is interesting and important. It has long been known that when dilute solutions of neutral salts are mixed there is no thermal change—heat is neither liberated nor absorbed. This is the well-known law of the thermoneutrality of salts. While the fact was established beyond question, and various suggestions had been made to account for it, it was generally conceded that no one of these was at all satisfactory. The explanation to-day is very simple. Take the two salts, potassium chloride and sodium nitrate; a dilute, aqueous solution of potassium chloride contains only

potassium ions and chlorine ions; a dilute solution of sodium nitrate contains sodium ions and nitric ions.



When the two solutions are mixed we have in the mixture potassium and sodium cations and chlorine and nitric anions, and nothing else. In a word, we have exactly the same ions in the mixture as in the solutions before they were mixed. There being no chemical change, there should be no thermal change, and such is the fact. The law of the thermoneutrality of salts could have been predicted from the theory of electrolytic dissociation, had it not been discovered long before the theory was discovered.

Colour of Solutions.—Another class of chemical phenomena which had long attracted attention, but the significance of which was not clearly understood, was the colour of substances, especially when in solution. Take, as an example, the colour of the permanganates. The salts of permanganic acid with the alkalis and alkaline earths all have apparently the same colour, which is the colour of permanganic acid itself. This was tested quantitatively by Ostwald, who photographed the absorption spectra of these and other permanganates where the cation was colourless, and showed that they all had exactly the same absorption bands. We can see at once the explanation of this fact. Permanganic acid dissociates thus:—



The colour of the solution is not due to the hydrogen ions, since there are hydrogen ions in solutions of all acids, and solutions of most acids are colourless. The colour of the solution of permanganic acid must be due to the presence of the permanganic ion:—



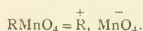
The colour of the solution of any permanganate in which the cation is colourless, is due to the ion:—



This can be seen at once, when we remember that any permanganate can be represented by the formula:—



in which R is a metal which yields a colourless cation. This compound would dissociate thus:—



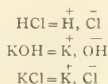
$\overset{+}{\text{R}}$ being colourless, the colour of the solution must depend upon the coloured ion:—



We thus see at once why all such salts of permanganic acid must have exactly the same colour.

Ostwald studied in all about 300 coloured compounds, and found the theory of electrolytic dissociation most helpful in explaining phenomena similar to the above.

Modes of Ion Formation.—We have spoken thus far of molecules breaking down into ions in the presence of a dissociating solvent:—



It must, however, not be concluded that this is the only way in which ions can be formed from molecules.

We may have one metal precipitated from a solution of one of its salts by another metal. When a bar of zinc is immersed in a solution of a copper salt, the zinc passes into solution and the copper is thrown out of solution. What

* From the *Journal of the Franklin Institute*, December, 1903.

takes place here is a transference of the electrical charge from the copper to the zinc. The copper having lost its charge, passes out of solution, while the zinc, having become an ion, passes into solution. This is obviously a mode of ion formation.

There are still other modes of ion formation. Take a bar of gold and dip it into chlorine water. Neither the gold nor the chlorine is in the ionic state before they come in contact. When they come in contact the gold becomes cationic and passes into solution, while the chlorine remains in solution, but passes from the molecular into the anionic condition. We have both cations and anions formed under conditions which are usually described as the solution of gold in chlorine water.

Solutions of Metals in Acids.—There are few chemical processes with which we are more familiar than the solution of metals in acids. Most metals dissolve in the strong acids, and from such solutions salts of the metals can be obtained on evaporation. This fact, which has been so long known, has only recently been satisfactorily explained. An acid dissociates, always yielding hydrogen ions, and anions whose nature depends upon the acid in question. This may be represented in general as follows:—

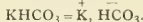
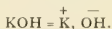


When such an acid is brought in contact with a metal, the hydrogen ions of the acid give up their charge to the metal, and escape as hydrogen gas. The metal, having taken the charge, passes into solution in the ionic state. This is a perfectly general process, independent of the nature of the acid and independent in general of the nature of the metal. In reality it is a mode of ion formation. An ion which holds its charge less firmly—hydrogen—giving it up to the metal which holds the charge more firmly, the hydrogen escaping in the gaseous condition, the metal passing into solution.

Hydrolytic Dissociation. Thus far the subject of electrolytic dissociation, or the breaking down of molecules into ions, has been considered. There is another kind of dissociation, which takes place in solutions of certain chemical compounds. When an alkali salt of a weak acid like carbonic acid is brought into the presence of water it shows an alkaline reaction. The fact has long been known, but no satisfactory explanation of it has been furnished. We have to-day a perfectly rational explanation of these and similar facts. There is at first a chemical reaction between the salt and the water, which takes place in the sense of the following equation:—



This is known as *hydrolytic dissociation*. As soon as the products of hydrolytic dissociation are formed they are electrolytically dissociated by the water. In the above case the following ions are formed:—



The hydroxyl ions from the dissociated water give the alkaline reaction, which is characteristic of such solutions.

We can thus see why the salts of weak acids react alkaline, and in a similar manner can understand why the salts of weak bases react acid. They are hydrolytically dissociated by water yielding the free acid, which then dissociates yielding hydrogen ions, which give the characteristic reaction to the solution.

Faraday's Law the Basis of Valence.—The lecturer then took up a discussion of Faraday's law as the basis of chemical valence. He pointed out that if we refer valence to the law of Faraday, we place it upon an exact physical basis. If we do not, the name valence is more or less indefinite, being used with a great variety of meanings.

Importance of Energy Changes for Chemistry.—The lecture concluded with a plea for the necessity of dealing with the energy changes which take place when substances react chemically. Hitherto we have regarded these energy

changes as subordinate, and have referred to chemical reactions as being accompanied by thermal change. This is confusing cause and effect. It would probably be much nearer the truth to say that thermal changes are accompanied by material transformations.

It was then pointed out that by studying material transformations alone we can never have an *exact science of chemistry*. This can be realised only by studying together with the products of the reaction, the thermal changes, the electrical changes, the light changes; in a word, the reciprocal transformations of intrinsic and other forms of energy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE. All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxviii., No. 4, January 23, 1904.

Fluochlorides, Fluobromides, and Fluoioidides of the Alkaline Earth Metals.—Ed. Defacqz.—The author shows that when a mixture of manganous fluoride is treated at temperatures between 800° and 1400° with chloride, bromide, and iodide of an alkaline earth, the alkaline earth fluoride results, together with the chloride, bromide, and iodide of manganese, the quantity of the latter increasing in proportion as the quantity of manganese fluoride is increased. He also shows that manganese chloride, bromide, and iodide react in the same way on alkaline earth fluorides. It follows therefore that, in the fused liquid, an equilibrium must be produced for the two reversible reactions. The transformation of manganous fluoride into an alkaline earth fluoride is only total when the quantity of chloride, bromide, or iodide of manganese, as compared with the alkaline-earth chloride, bromide, or iodide, is very small; the fluochlorides, fluobromides, and fluoioidides cannot then be formed, since they are destroyed by the chloride, &c., during fusion. Alkaline earth fluorides are formed when the manganous fluoride is mixed with a large excess of alkaline earth chloride, bromide, or iodide. Fluochlorides, fluobromides, and fluoioidides of the alkaline earths are also formed when the alkaline earth halides are entirely transformed into manganous chloride, bromide, or iodide by employing the theoretical quantities demanded by the equation $\text{MnF}_2 + 2\text{XY}_2 = \text{XF}_2 + \text{MnY}_2$; X representing Ba, Sr, or Ca, Y representing Cl, Br, or I.

Colour Reactions of Molybdc Acid.—Emm. Pozzi-Escot.—When a few drops of a solution of tannin is added to a solution of molybdc acid an orange solution is formed, becoming cherry-red in strong solution and yellow in dilute solution. This colouration constitutes a very sensitive test for molybdc acid, even showing with 1/100,000 part of ammonium molybdate in solution.

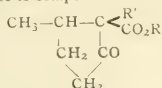
Electrolysis of Chloric Acid and Chlorates.—André Brochet.—The author investigates the mechanism of the action of copper on chloric acid and copper chlorate, both with and without the use of electrolysis, and elucidates the reactions—really simple, but apparently complex—which take place during the electrolysis of chlorates of the alkaline and alkaline-earth metals with a copper anode.

Trichlor-isopropyl Alcohol, $\text{Cl}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_3$.—Louis Henry.—The author completes the series of the methylation of the chlor-ethylic alcohols, and prepares trichlor-isopropyl alcohol, $\text{Cl}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_3$, by the reaction of anhydrous chloral on the magnesium compound of methyl iodide in ether. The substance when purified is crystalline, melting at 50–51° and boiling at 161.8° under a pressure of 773 m.m. It is interesting to notice the variation in properties in the series of trichlor-alcohols containing C_2 , C_3 , and C_4 .

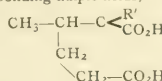
	Fusion.	Ebullition.
$\text{Cl}_3\text{C}-\text{CH}_2-\text{OH}$	17°	151°
$\text{Cl}_3\text{C}-\text{CH}-\text{OH}$	50°	161°
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \\ \\ \text{Cl}_3\text{C}-\text{C}-\text{OH} \end{array}$	96°	167°

Condensation of Acetylenic Ethers with Alcohols.
—Charles Moureu.—In a previous paper the author showed that methyl phenylpropionate, under the influence of sodium methylate in methylic alcohol solution, can fix 2 molecules of methylic alcohol, with formation of dimethylacetal of methyl benzoylacetate, by opening and completely saturating the acetylenic liaison, according to the equation—
 $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{CO}_2\text{CH}_3 + 2\text{CH}_3\text{OH} = \text{C}_6\text{H}_5-\text{C}(\text{OCH}_3)_2-\text{CH}_2-\text{CO}_2\text{CH}_3$.
This new reaction is now generalised, and the author studies from the same point of view the series of the acetylenic ethers.

α-Substituted β-Methyladipic Acids.—Marcel Desfontaines.—It is known that the β-methylcyclopentanonecarboxylic ethers behave with regard to sodium alcoholates and the alcoholic iodides as camphorcarboxylic ethers, giving rise to compounds of the form—



which, by a simple saponification with alcoholic potash, gives the corresponding adipic acids,—



The author prepares a series of these cyclic compounds and the corresponding di-substituted acids.

Certain Derivatives of Tetramethyldiaminophenyl-oxanthranol.—MM. Guyot and Stœhling.—In a previous research one of the authors established the fact that tetramethyldiaminophenyl-oxanthranol can easily attach itself to a certain number of products of the aromatic series without elimination of water. The present authors make analogous condensations with anisol and phenetol.

MEETINGS FOR THE WEEK.

- MONDAY, 29th.**—Society of Arts, 8. (Cantor Lectures). "Modern Book Printing," by Charles T. Jacobi.
TUESDAY, March 1st.—Royal Institution, 5. "Javanese Life and Character," by Ernest Foxwell, M.A.
Society of Arts, 4. 30. "Nigeria," by Lady Lugard (Miss Flora L. Shaw).
WEDNESDAY, 2nd.—Society of Arts, 8. "Physical Degeneration," by Robert Jones, M.D., &c.
Society of Public Analysts, 8. "Composition of Milk," by H. Doup Richmond, F.I.C. "Estimation of Morphine in Opium," by P. Schirowsky, Ph.D. "Iodine Absorption as a Factor in the Examination of Otto of Rosen," by F. Hudson-Cox, F.I.C., and W. H. Simmons.
THURSDAY, 3rd.—Royal Institution, 5. "Electrical Methods of Measuring Temperature," by Prof. H. L. Callendar, F.R.S.
Chemical, 8. "Chemical Dynamics of the Alkyl Iodides," by Miss K. A. Burke and F. G. Donnan. "Constitution of Phenolphthalein," by A. G. Green and A. G. Perkins. "Ketohydrobenzoic Acid," by W. H. Perkins, jun. "Photo chemically Active Chlorine," by C. H. Burgess and D. L. Chapman.
FRIDAY, 4th.—Royal Institution, 9. "Breathing in Living Things," by Prof. William Stirling, M.D., &c.
SATURDAY, 5th.—Royal Institution, 3. "The Life and Work of Stokes," by Right Hon. Lord Rayleigh, F.R.S.

TECHNICS.

A New Monthly Magazine for Technical Students.

No. 2 NOW READY.

PRICE 9d. net.

TECHNICS deals with all branches of Technology and Science. It records the progress of the technical and scientific world. Students, Professional Men, and that large section of the community anxious to be posted in the doings of the Technical world will find TECHNICS a reliable and indispensable magazine.

TECHNICS will be found invaluable to those who are engaged in the various branches of Technical study. Its articles are contributed by the greatest authorities on the subjects they write about. Some of the most eminent men connected with Technical Science have assisted us, and many more have promised their support and advice.

Some of the principal items to be found in No. 2 are—

THE PROGRESS OF SCIENCE AND TECHNOLOGY.

THE ROYAL COLLEGE OF SCIENCE, LONDON.

1. The Chemical Laboratories. By Prof. W. A. TILDEN, D.Sc., F.R.S.

2. The Physical Laboratories. By Sir ARTHUR RÜCKER, K.C.B., F.R.S. Illustrated from plans by Mr. ASTON WEBB, R.A.

GOING THROUGH the SHOPS. By JOSEPH G. HORNER, A.M.I.Mech.E.

THE PHOTOGRAPHIC IMAGE in THEORY and PRACTICE. By EDGAR SNYDER.

THE ELECTRO-CHEMICAL and ELECTRO-METALLURGICAL INDUSTRIES. Part I. Aluminium. By J. B. C. KERSHAW, F.I.C.

THE BACTERIOLOGY OF BREWING. By JAMES GRANT, F.C.S. THE CONTINUOUS CURRENT DYNAMO. Part II. By H. M. HOBART, M.I.E.E.

THE ELECTRIC and MAGNETIC PROPERTIES of ALLOYS of IRON. By Prof. W. E. HARRERT, F.R.S., and W. BROWN, B.Sc. INCANDESCENT ELECTRIC LAMPS. Part I. By Jas. SWINBURNE, M.I.C.E.

THE HEATING and VENTILATING of an EDUCATIONAL BUILDING. By W. W. F. FULLEN, A.M.I.C.E.

CONSTRUCTIONAL DESIGN. By E. FLANDER ETCHALLS.

ON THE DIAGRAMMATIC ILLUSTRATION of CLASS LECTURES. Part II. By WILFRID J. LINEHAM, M.I.C.E., M.I.M.E.

QUESTIONS & ANSWERS on SCIENCE & TECHNOLOGY, &c.

£200 and a GOLD MEDAL for the TECHNICS Prize-man.

Fully Illustrated by Photographs and Drawings.

GEORGE NEWNES, LIMITED,

3 TO 12, SOUTHAMPTON STREET, STRAND, LONDON, W.C.

CIVIL SERVICE COMMISSION.

FORTHCOMING EXAMINATION

Junior Assistant in the Department of the War

Office Chemist, Woolwich (20–25), 17th MARCH. The date specified is the latest at which applications can be received. They must be made on forms to be obtained, with particulars, from the SECRETARY, Civil Service Commission, Burlington Gardens, London, W.

The following Reminders of Stock are to be sold far below value:—

VALERAN ACID.
VALERIAN OIL and ETHER.
RUM ETHER, BUTIR ETHER,
FORMIC ETHER, FORMIC ACID,
SUBSTITUTE of LINSEED OIL.

C. D. RAMM, Hamburg 8, Germany.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half yearly

Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1s. 6d. each.

Volumes Bound in Cloth Cases, Lettered, and Numbered

at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.

FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.

LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO., 21, Mincing Lane, London, E.C., who hold stock ready for delivery.

MESSRS. LONGMANS & CO.'S SCIENTIFIC BOOKS.

TEXT-BOOKS OF PHYSICAL CHEMISTRY.

Edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S.

The PHASE RULE and its APPLICATIONS.

By ALEX. FINDLAY, M.A., Ph.D., D.Sc.,

Lecturer and Demonstrator in Chemistry, University of Birmingham. With 118 Figures in the Text, together with an

INTRODUCTION TO THE STUDY OF PHYSICAL CHEMISTRY,

By SIR WILLIAM RAMSAY, K.C.B., F.R.S., Editor of the Series.

Crown 8vo. 5s.

[Just Published.

•• SIR WILLIAM RAMSAY'S "INTRODUCTION TO PHYSICAL CHEMISTRY" is also issued separately, 1s net.

* * * *The Progress of Physical Chemistry is now so rapid, its domain is so extensive, and the number of journals devoted to its exposition is so great, that it has appeared desirable to issue a series of volumes, each of moderate compass, and each dealing with one branch of the subject. The rate of advance in various branches of the subject is not equal; while, for example, the basis of the science remains comparatively stationary (for methods of determining atomic and molecular weights, and the classification of compounds undergoes little modification), rapid progress is being made in other branches. Hence it has been thought proper to issue several short manuals, so that each individual one may be frequently brought up to date, independently of others. In this way, a statement of what is known on each subject will be made accessible to students and investigators. The subject has been divided as follows, among the authors mentioned:—*

- | | |
|---|---|
| An INTRODUCTION to PHYSICAL CHEMISTRY. By WILLIAM RAMSAY, K.C.B., F.R.S. 1s. net. [Ready. | STOICHIOMETRY. Professor SYDNEY YOUNG, D.Sc., F.R.S. |
| THE PHASE RULE. ALEXANDER FINDLAY, D.Sc. [Ready. | ELECTRO-CHEMISTRY. R. A. LEHFELDT, D.Sc. 2 Vols. |
| THE RELATION BETWEEN CHEMICAL CONSTITUTION AND PHYSICAL PROPERTIES. SAMUEL SMILES, D.Sc. | SPECTROSCOPY. E. C. C. BALY, F.I.C. |
| | THERMODYNAMICS. F. G. DONNAN, M.A., Ph.D. |
| | CHEMICAL DYNAMICS, and REACTIONS. J. W. MELLOR, D.Sc. |

The order in which these parts will be issued is not that given; for some subjects are more easily treated of than others; but it is hoped that all the volumes will be ready for the press before December, 1904.

A CHEMICAL CONCEPTION OF THE ETHER.

By D. MENDELEEFF,

Professor of Chemistry at the University of St. Petersburg.

Translated from the Russian by GEORGE KAMENSKY, A.R.S.M., of the Imperial Mint, St. Petersburg.

8vo. 2s. net.

[Just Published.

- A DICTIONARY of APPLIED CHEMISTRY.** By T. E. THORPE, B.Sc. (Vict.), Ph.D., D.Sc. (Dubl.), F.R.S., Professor of Chemistry in the Royal College of Science, London. Assisted by Eminent Contributors. Complete in Three Volumes, Half-bound. Vol. I., with 236 Illustrations, 8vo, £2 2s. Vol. II., with 240 Illustrations, 8vo, £2 2s. Vol. III., with 352 Illustrations, 8vo, £3 3s.
- A TEXT-BOOK of ELECTROCHEMISTRY.** By SVANTE ARRHENIUS, Professor at the University of Stockholm. Translated from the German Edition by JOHN MCCRAE, Ph.D. With 58 Illustrations, 8vo. 9s. 6d. net.
- FERMENTATION ORGANISMS: a Laboratory Handbook.** By ALB. KLÖCKER. Translated by G. E. ALLAN, B.Sc., and J. H. MILLAR, F.I.C. With 146 Illustrations in the text. 8vo. 12s. net.
- HIGHER MATHEMATICS for STUDENTS of CHEMISTRY and PHYSICS.** With Special Reference to Practical Work. By J. W. MELLOR, D.Sc., late Senior Scholar, and 1851 Exhibition Scholar, New Zealand University; Research Fellow, the Owens College, Manchester. With 142 Diagrams. 8vo. 12s. 6d. net.

LONGMANS, GREEN & CO., 39, PATERNOSTER ROW, LONDON, E.C.
NEW YORK, AND BOMBAY.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2310.

THE ELEMENTS: VERIFIED AND UNVERIFIED.*

By CHARLES BASKERVILLE, Ph.D., F.C.S.,
Smith Professor of General Chemistry, University of North Carolina

It is the sad duty of the retiring Chairman of this Section to chronicle the death of two members. One of them, James Francis Magee, B.S., University of Pennsylvania, 1887, devoted his life chiefly to commercial pursuits, in which he was most successful. He joined the Association at the fifty-first meeting, being one of our youngest. The other was H. Carrington Bolton, Columbia, 1862, (Ph.D., Göttingen, 1865), who, with the exception of four (Gibbs, Boyle, Brush, and Hilgard), was the senior of the Section, having joined at the seventeenth meeting. I beg permission to quote from an article of his in the *American Chemist*, 1876, the year following his elevation to Fellowship in the Association, as it exemplified, in telling words, one of the great aims in his life, with the fruitful accomplishment of which you are familiar:—

"So rapid are the strides made by science in this progressive age, and so boundless is its range, that those who view its career from without find great difficulty in following its diverse and intricate pathways, while those who have secured a footing within the same road are often quite unable to keep pace with its fleet movements, and would fain retire from the unequal contest. It is not surprising, then, that those actually contributing to the advancement of science, pressing eagerly upward and onward, should neglect to look back upon the labours of those who precede them and should sometimes lose sight of the obligations which science owes to forgotten generations."—"Notes on the Early Literature of Chemistry"—The Book of the Balance of Wisdom." New York Academy of Sciences, May 29, 1876.

His numerous contributions to and intimate knowledge of the history of chemistry, his gentle and generous sympathy, aided and stimulated many active in research or technical applications of chemistry. His monumental bibliographies put out by the Smithsonian Institution are masterpieces. The grief and keen regret of his loss are not confined to one nation.

On another occasion it has been the good fortune of him who has the honour of addressing you to-day to indicate that events of literary moment, governmental modifications, inventions, and forward stridings in science have apparently accommodated themselves to historical periods during the past century ("The Rare Earth Crusade—What it Portends, Scientifically and Technically," *Science*, N.S., xvii., 722; *CHEMICAL NEWS*, lxxxviii., 18). Striking novel facts and fancies, gleaned in the realm of inorganic chemistry, have crested not a few of the high waves of those human tides that beat against the coast of the untried and unknown.

The human mind knows by contrasts. For the day we have night, for the good there is evil. Where man would have a God, he also had a devil; for the true there is the false; the verified and unverified. The false may be true through ignorance; the true may be false in the light of new knowledge. Or, as Hegel put it, "Sein und das nicht Sein sind Nämliche."

Is matter continuous or discrete? argued the opposed schools of Grecian philosophy led by Leucippus, Democritus, and Epicurus, and dominated by Aristotle. Despite the clarity

of the statements of the Roman Lucretius,* the atomic hypothesis received scant attention until the Seventeenth century of the Christian Era, when Galilei's experimental science assailed Aristotelian metaphysics, and demanded verification of the promises of that philosophy which had governed all the schools of Europe for two thousand years (see "The Atomic Theory," the Wilde Lecture, by F. W. Clarke, at Dalton Celebration, May, 1903; *CHEM. NEWS*, lxxxii., 260¹). While Gassendi, Boyle, Descartes, Newton, perhaps Boscovich, Lavoisier, Swedenborg, Richter, Fischer, and Higgins had to do with our modern atomic theory, Dalton, one hundred years ago, "created a working tool of extraordinary power and usefulness" in the laws of definite and multiple proportions. As Clarke remarked (*loc. cit.*), "Between the atoms of Lucretius and the Daltonian atom the kinship is very remote." Although the lineage is direct, the work of Berzelius, Gmelin, and others,—the laws of Faraday, Gay Lussac, Avogadro, Dulong and Petit,—the reformations of Laurent and Gerhardt, but particularly Cannizzaro,—the systematisations of de Chancourtois, Newlands, Hinrichs, Mendeleef, and Lothar Meyer,—the stereo-chemistry of van't Hoff and Le Bel, have imperialised the ideas of the Manchester philosopher, so that the conceptions of the conservative atomists of to-day are quite different from those at the beginning of the closed century.¹

These have not come about solely through the additive labours of the savants mentioned, for they have been shaped quite as much by speculative and experimental opposition exemplified by Brodie ("Calculus of Chemical Operations," *Journ. Chem. Soc.*, 1866, xxi., 367; and his book "Ideal Chemistry," 1880) and Sterry Hunt (numerous papers summarised in "A New Basis for Chemistry," New York, 1887 and 1892, 4th edition).

In Graham's "Speculative Ideas respecting the Constitution of Matter" (*Proc. Roy. Soc.*, 1863) we have the conception that our supposed elements possess "one and the same ultimate or atomic molecule existing in different conditions of movement" (Venable, "The Definition of the Element," Vice-Presidential Address, Section C, A.A.A.S., Columbus Meeting, 1899). *Apropos*, we have the suggestion of F. W. Clarke, that the evolution of planets from nebule, according to the hypothesis of Kant and Laplace, was accompanied by an evolution of the elements themselves ("Evolution and the Spectroscope," *Pop. Sc. M. Journ.*, 1873). Even Boyle—"the cautious and doubting Robert Boyle," as Humboldt said of him—was inclined to the belief that "all matter is compounded of one primordial substance—merely modifications of the *materia prima*."

The Daltonian ideas had scarcely reached adolescence before Prout (1815), giving heed to the figures concerned, would have all the elements compounded of hydrogen. The classical atomic mass values obtained by sympathetic Stas and the numerous investigations of those who followed him, with all the refinements human ingenuity has been able to devise, temporarily silenced such speculations, but not until Marignac had halved the unit, Dumas had quartered it, and Zängerle, as late as 1882, insisted upon the one-thousandth hydrogen atom.

The notion, like Banquo's ghost, will ever up, for if one may judge from the probability calculations of Mallet (*Phil. Trans.*, 1881, clxxi., 1003) and Strutt (*Phil. Mag.*, [6], i., 311), a profound truth underlies the now crude hypothesis.

Crookes (*CHEMICAL NEWS*, 1886, lv., 83), from observations made during prolonged and painstaking fractionations of certain of the rare earths, supported his previously

* Nature reserving these as seeds of things—
Permits in them no minish nor decay.
They can't be fewer and they can't be less.

Again of compounds,—

Decay of some leaves others free to grow
And thus the sum of things rests unimpaired.

—*Id.* 11., 79.

¹ While I have examined much of the original literature, Venable's "History of the Periodic Law" has been most helpful. I have further, more, had the privilege of reading very carefully the manuscript of a work entitled "The Study of the Atom" (in press), by Dr. Venable.

* Address of the Vice-President of Section C (Chemistry) of the American Association for the Advancement of Science, St. Louis Meeting, December 28, 1903.

announced "provisional hypothesis" as to the genesis of the elements from a hypothetical *protyle* which existed when the universe was without form and void. He designated those intermediate entities, like yttrium, gadolinium, and didymium, "meta-elements"—a species of compound radicals, as it were (Address before Chemical Section of the British Association, CHEMICAL NEWS, 1883, liv., 117). *Urstoff*, fire-mist, protyle, the ultra-gaseous form, the fourth state of matter, was condensed by a process analogous to cooling; in short, the elements were created (Crookes, Royal Society, June 10, 1880). The rate of the cooling and irregular condensation produced "the atavism of the elements," and this caused the formation of the natural families of the periodic system. Marignac, criticising this hypothesis, states (*Archives des Sciences Physiques et Naturelles*, xvii., 5; CHEMICAL NEWS, lvi., 39):—"I have always admitted" the impossibility of accounting for the curious relations which are manifested between the atomic weights of the elements, except by the hypothesis by a general method of formation according to definite though unknown laws; even when these relations have the character of general and absolute laws."

Further, "I do not the less acknowledge that the effect of constant association of these elements is one of the strongest proofs that can be found of the community of their origin. Besides, it is not an isolated fact; we can find other examples, such as the habitual association in minerals of tantalum, niobium, and titanium."

Sir John Herschel thought that all the atoms were alike, and the elements, as we know them, "have the stamp of the manufactured article."

Hartley, this year, says (Address before the Chemical Section, British Association, Southport Meeting, Sept., 1903; CHEMICAL NEWS, lxxxviii., 154):—"It is more than twenty years since the study of homology in spectra led me to the conviction that the chemical atoms are not the ultimate particles of matter, and that they have a complex constitution."

The peculiar discharge from the negative electrode of a vacuum tube was investigated many years ago by Hittorf and Crookes, who arrived at the conclusion that it was composed of streams of charged particles. All are familiar with the very recent proposed "electrons" and "corpuscles" resulting from the beautiful physical researches of Lodge and J. J. Thomson. These appear to have caused a trembling in the belief of many in the immutability of the atom, and the complete abandonment of the atom is seriously discussed by others.

"If the electrons of all elements are exactly alike—or, in other words, if there is but one matter, just as there is but one force—and if the elements be but the various manifestations of that one matter, due to a different orbital arrangement of the electrons, it would seem that we are fast returning to the conceptions of the Middle Age alchemist. The transmutations of metals involves but the modification of the arrangement of the electrons." Such efforts as Fittica's ("Black Phosphorus, or Conversion of Phosphorus into Arsenic," CHEMICAL NEWS, lxxxi., 257; lxxxii., 166) should not be treated with scorn, but given the careful examination and merited consideration as Winkler gave his (*Berichte*, xxxiii., 10; CHEMICAL NEWS, lxxxi., 305). Science should thus ever be "a foe of raw haste, half-sister to delay" (Van Dyke in "The Ruling Passion").

Although by chemical means so far we have been unable to break up the atom, apparently electrical energy—in the form of cathode rays, for example—follows the grain of atomic structure. Some advanced thinkers look upon the atoms as disembodied charges of electricity. Ostwald has taught it. Electric charges are known only as united to matter, yet Johnstone Stoney and Larmor have speculated on the properties of such charges isolated. "Such a charge is inertia, even though attached to no matter, and the increase of inertia of a body due to electrification has been calculated by both Thomson and Oliver Heaviside, the

conception accordingly being advanced that all inertia is electrical, and that matter, as we know it, is built up of interlocked positive and negative electrons. If it were possible in any mass of matter to separate these electrons, then matter would disappear, and there would remain merely two enormous charges of electricity." We are aware of phenomena attributed to the negative electrons; we await anxiously the announcement of the positive electrons. But here the water is deep, and one may not swim too well.

We do know, however, as A. A. Noyes says ("General Principles of Physical Science," 1902, p. 13), that "there exists in the universe some thing or things other than matter, which, by association with it, gives rise to the changes in properties which bodies exhibit, and gives them power of producing changes in the properties of other bodies." Further (p. 15), "... matter is that which gives rise to the localisation of the complex of properties which certain portions of space exhibit. Even though, on the one hand, it must be admitted that the existence of matter is inferred only from various energy manifestations which bodies exhibit, it must be acknowledged, on the other, that there are no manifestations of energy except those which are associated with the manifestations of it that have led to the adoption of the concept of matter; in a word, the two assumed entities—matter and energy—are indissolubly connected in our experience." Thus, as Dumas said, "Hypotheses are the crutches of science, to be thrown away at the proper time."

I have dared to sketch these conceptions in a few bold outlines, for—

"We can't enumerate them all!
In every land and age have they
With honest zeal been toiling on,
To turn our darkness into day."*

(To be continued.)

SOME APPLICATIONS OF THE THEORY OF ELECTROLYSIS TO THE SEPARATION OF METALS FROM ONE ANOTHER.†

By A. HOLLARD.

In the present study I have co-ordinated a certain number of facts and experiments already published here and there in such a way as to bring them into line and show what philosophic bearing they have on one another. It thus clears the way for the presentation of an actual theory of electrolytic analysis that has not up to the present been put forward. The only principle involved hitherto in electrolytic analysis for the separation of elements is that which is based on the successive separation of the metals by gradual increase of the potential across the electrodes, each metal depositing itself at a potential spoken of as the potential proper to the metal.

Strictly speaking, this principle is hardly directly applicable. Indeed, it supposes the constant use of low potentials, and consequently small intensities, thereby prolonging the duration of the experiment. In fact, the only applications of this principle which have been made are the separations with very weak currents, of copper and silver, of silver and bismuth, and of mercury and bismuth, that is of metals whose polarisation potentials are lower than that of hydrogen.

As to metals with polarisation potentials higher than that of hydrogen (zinc, cadmium, iron, cobalt, nickel, tin, lead), they cannot be separated according to this same principle. In fact, the current, already very weak, which precipitates one of the metals, separates hydrogen from the bath just as much, and then the fraction of the current utilised for the deposit of the metal is so small, especially towards the end of the electrolysis, when the concentration

* Remarks made in 1860–65, after publication of Stas's "Researches on Atomic Weights," *Archives*, ix., 102, 24–376.

† Aikens' poem at Priestley centennial, *American Chemist*, 1875, 23.

† A Paper read before the Faraday Society, February 2, 1904.

of the metal ions becomes very low (Nernst's law), that the deposition of the metal is never complete. Thus zinc and nickel, which have a relatively large potential difference (0.54), have not been separated by us, when we used a slightly ammoniacal solution of the sulphates with a current of 0.01 ampère, the zinc always depositing itself with the nickel. We ought to work with a current of less than 0.01 ampère, seeing that a fraction only is utilised, but this would make the operation interminable.

Recognising that the foregoing principle is entirely insufficient, we have sought for other applications of the theory of electrolysis permitting of effectual analytical separations. The applications we have found will be ranged under three headings.

- I. Reduction of the resistance of the bath by suppressing the formation of gas at the anode.
- II. Influence of the nature of the cathode.
- III. Formation of complex salts. (This application has already been studied, especially by Frendenberg).

I Reduction of the Resistance of the Bath by suppressing the Formation of Gas at the Anode.

We have shown above that the metals whose polarisation potentials are higher than that of hydrogen cannot be separated from one another by gradual increase of the E.M.F., on account of the extremely small fraction of the current used to precipitate the metal. We have been able, however, considerably to increase the current by diminishing the resistance of the bath, and that in two ways.

1. By suppressing the liberation of oxygen at the anode.
2. By the use of soluble anodes.

1. To suppress the liberation of oxygen at the anode (or at least greatly to diminish it), we introduce a reducing agent into the bath, such as sulphurous acid, which prevents the liberation of oxygen gas by combining with it. This suppression of gas greatly augments the conductivity of the bath; for the same potential applied to the bath the current which passes is much more intense, and permits the precipitation of one of the metals on the cathode in a relatively short time.

Let us take a mixture of zinc and nickel, which cannot be separated by the application of the first principle; the sulphates of the metals are treated with sulphate of ammonia (10 grms.), sulphate of magnesium (5 grms.), 5 c.c. of a saturated solution of sulphurous anhydride, finally an excess of 25 c.c. of ammonia (sp. gr. 0.924). This is diluted to 300 c.c. and electrolysed at a temperature of about 90°, with a current of 0.1 ampère. The electrodes we used are shown in Fig. 1, the cathode being of platinum gauze, and sand-blasted.†

At the end of four hours at the most, for quantities of nickel which do not exceed 0.25 grm., 1—2 c.c. of the bath should not be blackened by ammonium sulphide. The electrolysis is allowed to continue for an hour, then the cathode is removed.

Experimental Results.

Quantities weighed.		Nickel deposited
Ni.	Zn.	
0.2500	0.05	0.2508
0.2500	0.1	0.2494
0.2500	0.25	0.2517
0.2500	0.5	0.2500
0.2500	0.5	0.2506
0.2500	1.0	0.2501
0.1000	0.1	0.0969
0.1000	0.5	0.0963
0.1000	1.0	0.0973

It is very important to adhere to the proportions of the reagents indicated, otherwise the separation may fail.

* It is important that the temperature should never fall below this value.

† These can be procured from des Moutons of London and Paris, and Pouleuc, of Paris.

Thus an excess of sulphurous acid leads to the formation of zinc sulphide.

This portion of the work was carried out with Mons. Bertiaux.

2. The use of a soluble anode to avoid the liberation of oxygen at the anode is less simple than the above procedure. On the other hand, the soluble anode in dissolving produces sufficient electric current to electrolyse the bath, and render the use of an external source of electricity unnecessary.

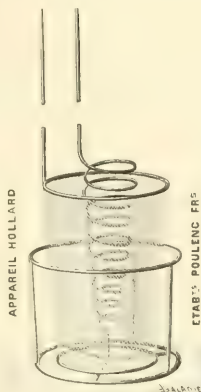


FIG. 1.

The metal selected for the anode should be of such a nature that it can replace in the solution the metal that is to be separated, and that only. In order that this may not be precipitated on the anode, but only on the platinum cathode, the anode must be immersed, not in the bath, B, itself (Fig. 2), but in the solution A containing an indifferent salt (salt of an alkali or an alkaline earth) separated from the bath B by a membrane of vegetable parchment.

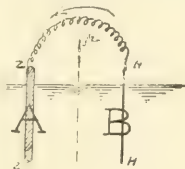


FIG. 2.

If it is required to separate nickel from zinc, we make use of a zinc anode. We take a vessel separated into two cells by a membrane of vegetable parchment (paper treated with sulphuric acid). We place in one of the cells, B, the solution containing the nickel and the zinc, and in the other, A, a salt solution, which must be a conductor of the current—a solution of magnesium sulphate serves very well. The zinc sheet intended to precipitate the nickel is immersed, not in the solution B containing the nickel, but in the magnesium sulphate solution. In the solution B, a sheet of platinum H N is placed. Finally, the platinum and zinc are connected by an external copper wire. We thus make a reversible cell of two liquids of the Daniell type, in which the current goes from the platinum to the zinc by an

external conductor, and from the zinc to the platinum in the interior of the liquid.

We will therefore examine an actual electrolysis of a nickel salt, giving a deposit of pure nickel on the platinum sheet :—

In practice we proceed as follows :—

The nickel and zinc in the state of soluble sulphates are contained in a Bohemian beaker (650 c.c. capacity, 7 c.m. diameter). This solution should contain an excess of 20 c.c. ammonia, 22° Bé., and 100 grms. of anhydrous ammonium sulphate, and should occupy a volume of 250 c.c.

Obviously this liquid is a good conductor of the current. We put into it our electrode of platinum gauze (Fig. 3). A glass tube 55 m.m. internal diameter, closed at the base by a membrane of vegetable parchment, is immersed in the solution of nickel and zinc in the beaker, so that the membrane is as near as possible to the electrode without, however, touching it. A solution of magnesium sulphate,

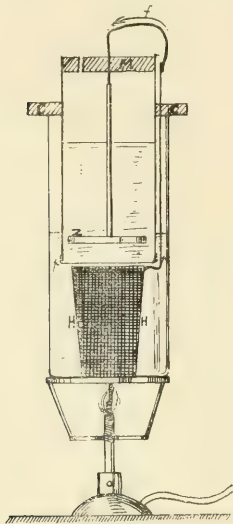


FIG. 3.

250 grms. to the litre, is poured into the tube to fill it to a depth of about 70 m.m. This strength of magnesium sulphate solution possesses the maximum conductivity. The choice of this salt as conductor for the inner cell is that it is one of the few salts which have no chemical action on zinc.

Finally, an amalgamated zinc disc, 5 c.m. diameter, attached to a rod of copper insulated by caoutchouc, is immersed in this liquid. The copper rod is connected externally to the platinum electrode. The zinc disc is pierced with several holes to facilitate the circulation of the inner cell liquid, and placed 15–20 m.m. above the parchment.

During the whole of the experiment, the contents of the outer cell are heated nearly to boiling (about 95°). At the end of several hours the nickel is completely deposited on the electrode as a fine, strongly adherent metallic layer. The electrode is withdrawn, swilled with water, then plunged into distilled water for ten minutes to complete the washing, finally dried and weighed.

Experimental Results.

Quantities taken.		Nickel deposited.	
Ni.	Zn.		
1	0.2000	1	0.2026
2	0.2000	0.5	0.1995
3	0.2500	1	0.2499
4	0.2500	1	0.2525
5	0.5000	0.0	0.4989
6	0.4500	1	0.4506
7	0.5000	1	0.5048
		(contained a little zinc)	
8	0.0500	1	0.0524

One sees from the above table that the method can be applied to varying proportions of zinc and nickel. On the other hand, the mixture should not contain more than 1 grm. of zinc or 0.45 grm. of nickel, otherwise the simultaneous deposition of zinc becomes possible.

Experiment 7 shows that already with 0.5 grm. of nickel and 1 grm. of zinc, there is a deposition of zinc. When there is no zinc in solution at least 0.5 grm. pure nickel can be deposited (Experiment 5).

These limits as to the quantities of nickel and zinc find their explanation in the theory of the method we are about to give. This theory is none other than that of reversible cells.

The solution-pressure P of the precipitating metal* (in this case zinc) being higher than the solution-pressure P_1 of the precipitated metal† (here nickel), a positive E.M.F. is established between the two metals, according to Nernst's formula :—

$$(1) \quad e = \frac{K}{v} \log \frac{P}{C} - \frac{K}{v_1} \log \frac{P_1}{C_1}$$

K is a constant for a definite temperature, v and v_1 are the valencies of the precipitating and precipitated metals, C and C_1 the concentrations of the two metals.†

One sees, according to this formula, that when the concentration C of the zinc in the inner cell increases (consequent upon the deposition of nickel on the platinum electrode) e will diminish. It is necessary then that there should not be too much nickel to deposit; 0.45 grm. can, however, be easily deposited. According to the same formula, if the concentration of the nickel diminishes, e tends towards zero, which means that the nickel can never be completely deposited. This would indeed happen if we were working with a solution of the normal sulphate of nickel, but we work with a solution containing a large excess of ammonia; that is, a solution containing a large concentration of the ions NH_4^+ ; thus C_1 does not represent the concentration of the nickel ions, but a mean of the concentration of the ions Ni^{++} and NH_4^+ . This ammonium gives rise to a disengagement of hydrogen during the electrolysis.

Therefore, when one would generalise this method for other separations than that of nickel and zinc, care must be taken to put into the solution an excess of ammonia or acid, or any other substance capable of forming hydrogen ions, or ions playing the same part.

In reality, the phenomenon is complicated by secondary reactions which it will be always necessary to take into account when it is desired to extend the method to other separations than that of nickel and zinc.

1. The concentration of the zinc sulphate should not be too great, for then this salt on the one hand and the dilute

* The idea of solution-pressure has been suggested in the ionic theory by the analogy which has been established between the tendency which bodies have of becoming ionised, and the tendency which bodies have of passing into the state of vapour. Just as the measure of the second is called the vapour-pressure, so the first has been called the solution-pressure.

† The order of the solution-pressures is the same as that of the polarisation potentials.

‡ In the Nernst formula we have put C and C_1 as the concentration of the metals, in place of their osmotic pressures p and p_1 , which should have been used, because C and C_1 are proportional to p and p_1 on account of the relatively great dilution of the solutions we have employed.

solution of zinc sulphate which is formed on the other hand by the solution of the zinc in the inner cell, will form a concentration cell ($Zn | ZnSO_4 \text{ dilute} || Pt | ZnSO_4 \text{ concentrated}$; Zn and Pt representing the poles of the cell, that is, the zinc disc and the platinum electrode). Otherwise the total E.M.F. of the system may reach such a point that the zinc can be precipitated with the nickel, which we found to be the case when the nickel was accompanied by 2 grms. and more of zinc. That is why we have recommended that there should not be more than 1 gm. of zinc in the nickel solution.

2. The sulphate of zinc formed in the solution of magnesium sulphate by the solution of the zinc, attacks the disc of zinc, especially when warm; hence a voltaic couple which produces a new increase of the E.M.F.; an increase which we have endeavoured to diminish as much as possible by arranging the cell so that the disc is in the coolest part of the apparatus. The concentration of zinc sulphate increases as the nickel is deposited, causing the attack on the zinc disc and the E.M.F. to become greater; this would end by favouring the deposit of zinc with the nickel. Fortunately this concentration decreases the E.M.F. of the concentration element spoken of in the previous paragraph, as well as the E.M.F. of the principal element (see Nernst formula), so that one can easily deposit 0.45 gm. of pure nickel even when accompanied by 1 gm. of zinc. When nickel alone is present, one can deposit still more, for in this case there is no concentration element. Hence it follows that the quantity of pure nickel that can be deposited is greater as the accompanying zinc is less (for then the effect of the concentration element is reduced), and inversely that the quantity of zinc accompanying the nickel can be greater according as the nickel is present in smaller amount (for then the E.M.F. of the cell is reduced). By not having more than 0.45 gm. of nickel and 1 gm. of zinc in the solution, one is always certain to have pure nickel deposited.

3. Finally, there is another secondary phenomenon which does not occur with nickel sulphate, but which is manifest with certain other salts. This can be discussed for the sake of completeness. We mean the migration of the salts in the course of the electrolysis from the cathode (here the platinum electrode) to the anode (here the precipitating metal). This is Hittorf's phenomenon. For each metal, then, it is necessary to find out if it forms a salt which does not show the Hittorf phenomenon, and if it is preferable to work at one temperature more than another, for the losses in concentration round the cathode (and around the anode) vary with the temperature. The method cannot be applied to every class of salt, and so is not general. It cannot be used for copper in particular, the Cu^{++} ions passing very rapidly to the anode cell.

(To be continued).

ESTIMATION OF PERSULPHATES.

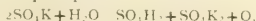
By C. MARIE and L. J. BUNEL.

THE methods in use up to the present for the estimation of persulphates can be divided into two groups:—

1. Those which are based on the oxidising power of the salt.
2. Those which depend on the estimation of the acid liberated during their decomposition.

Le Blanc and Eckardt, Mondolfo, Grutzner, and others have all proposed various methods; while Peters and Moody, who have made comparative tests of them all, do not consider the iodometric methods of Mondolfo and Namias to be exact, but they recommend the methods of Le Blanc and Grutzner.

More recently Taruggi has proposed the acidimetric estimation of the sulphuric acid set free during the decomposition of the persulphate in the reaction:—



The author uses phthalein for the titration, and considers that a total decomposition may be effected by boiling for twenty minutes.

In the case of persulphate of ammonia, it is necessary to operate in the presence of an amount of titrated soda sufficient to replace the ammonia of the salt. By proceeding differently we obtain erroneous results; we shall refer to this question later on.

Now, in undertaking these experiments with the object of examining the quantitative formation of persulphates by electrolysis, we found that the time of boiling mentioned was insufficient to obtain the complete decomposition of the persulphate.

We prepared a decinormal solution of pure dry persulphate of potassium. The estimation of the potassium on a portion gave for 1 molecule of SO_4K :— $K = 38.8$ found, 39 theory. Twenty-five c.c. were boiled for fifteen minutes, cooled, and titrated with methyl-orange; the titration being made in the cold, the decomposition of the salt does not continue.

The neutralised solution is again boiled; every five minutes it is cooled and titrated; this is repeated for forty minutes. The results are given in the following table:—

SO_4K N/10	Time of boiling	$NaOH$ N/10
C.c.	Mins.	
25	15	18.5
25	20	23.9
25	25	24.6
25	30	24.8
25	35	25.05
25	40	25.05

The experiments repeated with sodic and ammoniac persulphates gave the same results; thus, a minimal boiling of thirty-five minutes is necessary to bring about the complete decomposition of an alkaline persulphate in aqueous solution. In this manner we have been induced to examine the action of a large number of bodies with the object of finding one which would accelerate the decomposition of the persulphate; methylic alcohol has given us the best results.

If we treat a solution of a persulphate with methylic alcohol in excess and then boil, the persulphate transforms a portion of the alcohol into aldehyde, according to a well known reaction. We have made quite certain that no formic acid is formed.

We have tested this method with the pure persulphates of potassium and ammonium; compared with that of Le Blanc and Eckardt, this method has given the most concordant results. The results are given in the following table:

SO_4K N/10	Alcohol	Time of boiling	$NaOH$ N/10
C.c.		Mins.	
25	2	15	44.9—25.05
25	2	25	24.9—25.05
25	20	15	24.95
SO_4NH_4 N/10			
25	2	15	44.9—25.0
25	20	25	25.0

By this method we have titrated impure persulphate of soda and found:—

	By our method	By Le Blanc's method
SO_4Na , per cent . .	87.5	87.4

These results justify us in recommending the following procedure for the titration of alkaline persulphates:—

Dissolve about 0.3 to 0.4 gm. of the sample in 100 c.c. of water; neutralise the solution, which is generally acid, in the presence of methyl-orange; then add 2 c.c. of methylic alcohol, heat for five minutes to 70–80°, and then boil for ten minutes, cool, and titrate with methyl-orange and decinormal soda.

1 c.c. of decinormal soda corresponds to 0.0135 gm. SO_4K	
1 " " " " " " " " " " " "	0.0110 " SO_4Na .
1 " " " " " " " " " " " "	0.0114 " SO_4Am .

We have already seen that in the titration of persulphate of ammonia, M. Taruggi recommends boiling the solution treated with a sufficient quantity of titrated soda to completely displace the ammonia in the salt.

Without taking this precaution we obtain results much too high; for example:—

SO ₄ NH ₄	N/10.	Time of boiling.	NaOH N/10.
C.c.			
25		15 mins.	26.8 (theory 25)
25		20 "	27.6
25		1 hour	28.85

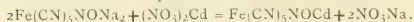
This does not occur in the presence of methylic alcohol. We think it is correct to attribute this fact to the oxidation of the ammonia, which is transformed into nitrogen and water by the oxygen of the persulphate.

In fact, if we boil a solution of persulphate of ammonia in a vessel traversed by a current of carbonic acid, and collect the gases given off in a solution of potash, we find a considerable residue of nitrogen after absorbing the oxygen with an alkaline pyrogallate. If this phenomenon is not produced in the presence of methylic alcohol, it is because the speed of oxidation of the ammonia is very slow compared with that of the alcohol. This, however, requires further study, which we propose to carry out.—*Bull. Soc. Chim.*, Series 3, vol., xxix., No. 18.

VOLUMETRIC ESTIMATION OF THE ALKALINE NITROPRUSSATES, AND OF THE SOLUBLE SALTS OF CADMIUM.

By MM. FONZES-DIACON and CARQUET.

The volumetric estimation of a soluble nitroprussiate is based on the following principle:—Nitroprussiate of cadmium being insoluble in water, if to a solution of a nitroprussiate we add a known volume of a titrated solution of nitrate of cadmium, a precipitate will be formed containing the whole of the nitroprussiate:—



Thus by estimating volumetrically the excess of nitrate of cadmium, we can determine the weight of the corresponding nitroprussiate; but we might also estimate this latter compound directly by the volumetric analysis of the precipitated nitroprussiate of cadmium.

These two methods will serve as a check on each other, and we can take the mean of the two observations.

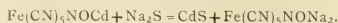
1. *Estimation of the Excess of Nitrate of Cadmium.*—We first prepare a titrated solution of this salt by dissolving 8 or 10 grms. in a litre of water, and determining the value volumetrically by means of a titrated solution of sulphide of sodium, using a few drops of nitroprussiate of soda as an indicator, $(\text{NO}_3)_2\text{Cd} + \text{SNa}_2 = \text{SCd} + 2\text{NO}_3\text{Na}.$

At first a yellow precipitate of sulphide of cadmium is formed, and the end of the reaction is shown by the appearance of the violet colouration caused by the action of a slight excess of sulphide on the nitroprussiate of soda.

We then add to a known volume of the nitroprussiate solution under examination a known excess volume of the titrated solution of nitrate of cadmium; the precipitate is separated by filtration and washed, and in the filtrate mixed with the washings we estimate volumetrically the excess of nitrate of cadmium; for this purpose we add a few drops of nitroprussiate, and, by means of a burette, add the titrated solution of sulphide of sodium until a violet colour appears.

2. *Analysis of the Nitroprussiate of Cadmium.*—The precipitate collected on the filter is dissolved in a little ammoniacal water; into this solution we pour, drop by drop, a titrated solution of sulphide of sodium; there is first formed a yellow precipitate of sulphide of cadmium, and at the end of the operation there appears the violet colour-

ation caused by a slight excess of sulphide on the nitroprussiate of soda formed:—



The verification of the sensitiveness of this method has shown us that it has all the accuracy required of a volumetric method.

It is of general application, except always in the presence of cyanides and of ferro- and ferri-cyanides; we can, however, get rid of the former by passing a current of carbonic acid gas through the boiling solution; this drives off the hydrocyanic acid, and we can then precipitate the latter salts by the addition of sulphate of zinc. In the filtered solution we can estimate the nitroprussiate by the above mentioned method.

This method has enabled us to detect and estimate nitroprussiate of soda in the organism during a series of experiments undertaken to determine the toxicity of this salt.

Thus, this method is applicable also to the volumetric estimation of a soluble salt of cadmium; for this purpose we use a titrated solution of sulphide of sodium in the presence of nitroprussiate of sodium, which serves as an indicator.—*Bull. Soc. Chim.*, Series 3, vol. xix., No. 13.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, February 17th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

Mr. E. R. BUGGÉ was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William Barbour, M.A., B.Sc., Grove Villa, Waltham Cross; R. H. Durward Benn, Westmount, Montreal, Canada; Ellis Clayton, 6, Spring Hurst Road, Saltaire; Percy Kent Le May, 6, Lothair Villas, Hatfield, Herts; Franklin E. Robertson, Harders Road, Peckham, S.E.; Thomas G. Shacklady, Addiscombe Villas, Cliffe-at-Hoo, Kent.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As Treasurer: Dr. A. Scott, F.R.S., *vice* Dr. H. T. Brown, F.R.S.

As Secretary: Dr. M. O. Forster, *vice* Dr. A. Scott, F.R.S.

As Vice-Presidents: Dr. H. T. Brown, F.R.S., and Prof. H. B. Dixon, F.R.S., *vice* Prof. H. McLeod, F.R.S., and Prof. H. A. Miers, F.R.S.

As Ordinary Members of Council: Dr. Bernard Dyer, Mr. A. D. Hall, Dr. A. Lapworth, Prof. J. M. Thomson, F.R.S., *vice* Dr. M. O. Forster, Mr. S. U. Pickering, F.R.S., Dr. J. A. Voelcker, and Prof. J. Walker, F.R.S.

Dr. L. T. Thorne, Dr. G. T. Moody, and Dr. J. Wade were elected to audit the Society's accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—John Prest Ackroyd, B.Sc.; Allen Baguley, B.Sc.; Charles Thomas Bennett; Alick Cole Benson; George Edward P. Broderick, B.Sc.; Alfred Denys Cowper; Julien Drugman, Ph.D.; Nevil Norton Evans; James Rocheid Forrest; George Fry; Robert Gawler, M.Sc.; Anu Ghose; Harry James Glover; John Augustus Goodson; John Monteath Guthrie; Leo Frank Guttman, Ph.D.; Alfred Henry Hoyt; Cyril Douglas McCourt; Francis D'Oyley Mears, jun.; Bernard Middleditch, B.A.; Jack Percival Montgomery; Benjamin L. Murray, B.S.; Thomas S. Patterson, Ph.D.; Bertram Prentice, Ph.D., D.Sc.; Jatindranath Sen, M.A.; Alfred Shrubsole; Raymond Louis Siau; Samuel John Smith; Henry Ernest Stevenson; Frederick Henry Streatfeild; Charles Edward

Thompson, Alfred Thompson, B.Sc.; Alfred Tingle, B.Sc., Ph.D.; William Wood Underhill; Leon Edward Walling; Francis Langston Watt; Charles Edward Whiteley; William Henry Woodcock.

Of the following papers, those marked * were read:—

*21. "Observations on some Interfacial and Originally Reversible Changes Extending over Prolonged Periods of Time." By RICHARD JOHN FRISWELL.

The question of the limitation of chemical action to a certain range of temperature was discussed in the light of W. R. Grove's experiments on the dissociation of water by heat, described in the Bakerian Lecture (*Phil. Trans.*, 1847, cxxxvii., 1), and of recent experiments at very low temperatures, and it was pointed out that, as a rule, reactions are hastened by elevation of temperature, and hence their course has been less studied than their products.

Reference was made to V. Meyer's labile hydrogen atom, and some results obtained by the author and A. G. Green (*Trans.*, 1885, XLIV., 917; 1880, XLII., 749) were discussed. It is suggested (1) that the labile condition is not confined to hydrogen; (2) that the constitution of a compound is only relative, and exists only so long as the substance is submitted to a certain definite stress; (3) that different stresses develop dissimilar constitutions, and that therefore the constitution of a compound depends on its environment.

Experiments on the changes occurring during very long periods of time were described, these consisting in the slow appropriation by aminoazobenzene base from a solution of aniline hydrochloride of sufficient hydrochloric acid to saturate itself; this reaction was shown to occur even in the presence of much free aniline, and the variations due to changes of temperature were described.

These and analogous experiments are held to justify the arguments as to the effects of stress on the successive disruption of the molecules of aniline hydrochloride and aminoazobenzene hydrochloride.

Preparations illustrating the above-described experiments were exhibited.

DISCUSSION.

Dr. MORGAN suggested that the interaction occurring between aniline hydrochloride and aminoazobenzene might be explained in terms of the ordinary theories of chemical equilibrium.

Aniline hydrochloride, in aqueous solution, undergoes dissociation, and attains a state of equilibrium, which may be represented approximately by the equation $C_6H_5 \cdot NH_3Cl \rightleftharpoons C_6H_5 \cdot NH_2 \cdot HCl$. This equilibrium is disturbed by the introduction of aminoazobenzene, because this base forms a sparingly soluble hydrochloride, and thus gradually abstracts the free acid from the solution. Excess of aniline hinders this change owing to the fact that, being itself a product of the dissociation of the soluble hydrochloride, it reverses the foregoing balanced reaction, in accordance with the law of mass action, thereby decreasing the amount of available hydrochloric acid.

Dr. HEWITT asked whether the proof of the existence of a diazonium salt in an acid solution of diazoaminobenzene during the period of isomerisation to aminoazobenzene did not depend on the coupling properties of such a solution; if so, the demonstration is not conclusive, since it has been known for years that diazoamino-compounds couple with phenols even in the absence of acids. One of the earliest known cases of this reaction was discovered by Heumann and Economides, who obtained benzeneazophenol from diazoaminobenzene and phenol (*Ber.*, 1887, xx., 372).

In reply to Dr. Hewitt, Mr. FRISWELL said that a full account of the evidence for the presence of diazobenzene chloride in the solution during the conversion of the diazoaminobenzene into aminoazobenzene would be found in the papers published in conjunction with Prof. A. G. Green (*loc. cit.*). Shortly, it consisted in treating the separated solution with phenols and amines, whereby known azo-dyes were produced and identified.

In reply to Dr. Morgan, he had no objection to make to

the explanation based on the suggested tendency to dissociation of aniline hydrochloride in aqueous solution. He had endeavoured to overcome this tendency by the addition of free aniline, but this only delayed the abstraction of the acid by the aminoazo-base, and, in his opinion, furnished additional evidence in favour of the stress hypothesis which he had advocated.

*25. "Note on Magnesium Oxybromide." By GEORGE WILLIAM FRISWELL HOLROD.

An ethereal solution of magnesium phenyl bromide, obtained by Grignard's method (*Ann. Chim. Phys.*, 1901, xxiv., 437), when saturated with acetylene and left in a stoppered vessel for several days, deposited clear, colourless crystals having the form either of octohedra or of combinations of the octohedron and cube. The yield of crystals was about 4 grms. from 50 grms. of bromobenzene.

The volume of the solution before passing the acetylene was 220 c.c., and 52 grms. of bromobenzene were employed. The acetylene, dried with phosphorus pentoxide, was passed through successive portions of 30 c.c. of this solution, the current of gas being continued for about four hours, and the flasks being kept for two or three days or longer before removing the crystals which are gradually deposited. The ethereal solution diminished to about two-thirds of its original volume during the saturation with acetylene.

The crystals, which vary considerably in size when obtained from distinct preparations, are hygroscopic and very soft; they were not re-crystallised for analysis, but rapidly dried on filter-paper, scraped with a sharp nickel spatula, and analysed as quickly as possible.

0.1047 gave 0.1291 $AgBr$. Br 53.00.
0.0894 " 0.0458 $MgSO_4$. Mg 10.86.
 $C_{12}H_{10}O_2Br$ requires Br 52.86; Mg 10.49 per cent.

The substance is decomposed by water, heat being generated during the reaction; magnesium hydroxide is precipitated, and ether is set free.

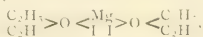
The ether was estimated by introducing a crystal into a eudiometer standing over mercury; dry oxygen and two drops of water were then added successively, the apparatus was surrounded by a steam jacket and an electric spark passed through the gaseous mixture. The carbon dioxide produced was measured by caustic potash absorption, after decomposing any magnesium carbonate present by the addition of three drops of dilute sulphuric acid.

0.0221 gave 8.44 c.c. CO_2 ; $Mg_2Br_3 \cdot C_8H_{21}O_3$ requires 8.73 c.c. CO_2 .

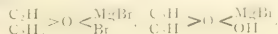
Oxygen used = 13.34 c.c.; $Mg_2Br_3 \cdot C_8H_{21}O_3$ requires 13.1 c.c. oxygen.

The analyses point to the formula $Mg_2Br_3 \cdot OH, 2(C_2H_5)_2O$, and the substance doubtless owes its origin to the action of small quantities of water on the magnesium phenyl bromide, $C_6H_5 \cdot MgBr + H_2O = C_6H_5 \cdot Mg \cdot OH$, the magnesium oxybromide then combining with ether and magnesium bromide; the latter is always a by-product of the action of bromobenzene on magnesium in ethereal solution, the acetylene serving merely to evaporate the ether.

Zelinsky (*Chem. Centr.*, 1903, ii., 277), by the interaction of magnesium, iodine, and ether, obtained a compound to which he assigns the formula—



and the compounds $MgBr_2 \cdot 3(C_2H_5)_2O$ and $MgBr_2 \cdot 4(C_2H_5)_2O$ have also been produced. Zelinsky considers that these compounds play the rôle of catalysts in the formation of the mixed organo-magnesium compounds. The compound obtained by the author is evidently related to these products, and should perhaps be represented by the formula



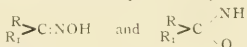
*26. "The Arrangement in Space of the Groups combined with the Tervalent Nitrogen Atom." By FREDERIC STANLEY KIPPING and ARTHUR HENRY SALWAY.

The Hantzsch and Werner hypothesis regarding the tervalent nitrogen atom indicates the existence of enantiomorphously related isomerides in compounds of the type $\text{NR}_1\text{R}_2\text{R}_3$, and one of the objects of this investigation was either to isolate, if possible, such isomerides or to demonstrate their non-existence.

Since an externally compensated acid chloride may be used for the detection of asymmetry in bases where the asymmetry is due to a carbon atom (Kipping and Hall, *Trans.*, 1901, lxxix., 444), it seemed probable that, if tervalent nitrogen compounds were asymmetrical, their asymmetry could be detected in like manner, but no evidence of the existence of isomerides was obtained on examining the products of the interaction of *dl*-benzylmethylacetyl chloride with methylaniline, *p*-toluidine, benzylaniline, and phenylhydrazine. *p*-Toluidine and benzylaniline also gave negative results with optically active benzylmethylacetyl chloride. Although the introduction of one centre of asymmetry failed to afford separable isomerides, it seemed highly probable that the introduction of a second centre of asymmetry would give a satisfactory result if enantiomorphously related derivatives of tervalent nitrogen were really capable of existence. The products from *d*-benzylmethylacetyl chloride and *l*-methylamine, *d*-hydrindamine, *l*-methylhydrindamine, and *l*-phenylethylamine, however, retained their uniform character after fractional crystallisation. These results indicate that the three radicals, together with the tervalent nitrogen itself, are situated in one plane; that two of the radicals are symmetrically arranged with respect to the third, and that in all probability this is true of any two; that is to say, the whole arrangement is the most symmetrical one possible.

The substituted amides derived from the interaction of benzylmethylacetyl chloride and the foregoing inactive and active bases were described.

Assuming that the isomerism of the syn- and anti-forms of oximes is structural and represented by the formulæ:—



the latter structure, since it contains an asymmetric carbon atom, should exist in enantiomorphously related forms, and the introduction of an optically active acid chloride should produce two non-enantiomorphously related separable isomerides. The action of benzylmethylacetyl chloride on benzoinoxime was studied, but instead of the desired acyl derivative, the following products were obtained:—Benzil, benzoin, benzaldehyde, benzonitrile, ammonium chloride, hydrogen chloride, and benzylmethylacetic acid, together with a compound melting at 126° . Attempts to obtain a benzylmethylacetyl derivative from *a*-benzaldoxime were also unsuccessful, decomposition taking place with the formation of benzonitrile.

Benzoyl chloride interacts normally with benzoinoxime, giving benzoinoxime benzoate, $\text{CHPh}(\text{OH})\text{CPh}:\text{NOBz}$, which crystallises from alcohol in leaf-like plates melting at $165-166^\circ$.

Benzoylbenzoinoxime, $\text{CHPh}(\text{OBz})\text{CPh}:\text{NOH}$, prepared by treating benzoylbenzoin with hydroxylamine, crystallises from alcohol in globular clusters melting at 148° .

dl-Benzylmethylacetyl chloride gives, with *dl*-hydrindamine two isomeric *dl*-benzylmethylacetylhydrindamines, which can be easily separated; these two compounds melt at $110-111^\circ$ and 119.5° respectively, and their formation affords proof of the asymmetry of the hydrindamine molecule.

d-Benzylmethylacetyl chloride and *dl*-hydrindamine give a mixture of the isomeric amides *dAdB* and *dAlB*, from which the derivative of the *d*-base is easily isolated; the enantiomorphously related components of *dl*-*a*-phenylethylamine may be separated in a similar manner, the com-

pound, $\text{CH}_2\text{Ph}\cdot\text{CHMe}:\text{CO}\cdot\text{NH}\cdot\text{CHMePh}$, of the *l*-base being easily isolated.

27. "The Esterification of *r*-Mandelic Acid by Menthol and Borneol." By ALEXANDER MCKENZIE.

The results recorded in this research deal with the method of resolving *i*-compounds devised by Marckwald and the author (*Ber.*, 1899, xxxii., 2130; 1900, xxxiii., 208; 1901, xxiv., 459. Compare Walden, *Ber.*, 1899, xxxii., 2703; E. Fischer, *Ber.*, 1899, xxxii., 3617).

When *r*-mandelic acid was heated with *l*-borneol, the unesterified acid was levorotatory, whilst the mixture of esters yielded a levorotatory acid. When *l*-bornyl *dl*-mandelate was submitted to fractional hydrolysis, a levorotatory acid was obtained from the initial hydrolysis, and an inactive acid from the final hydrolysis of the residual esters by an excess of alcoholic potassium hydroxide. *d*-Mandelic acid was isolated from the dextrorotatory acid obtained from the initial hydrolysis of *l*-menthyl *dl*-mandelate. *l*-Menthyl *dl*-mandelate can yield either a dextrorotatory or a levorotatory acid from the initial fractional hydrolysis according to the amount of alkali used. *l*-Menthyl *dl*-mandelate boils at 225° under 30 m.m. pressure, and melts at $85-86^\circ$; it has $[\alpha]_D^{18} -74.2^\circ$ ($c=10.890$) in ethyl-alcoholic solution; it is partially racemic, and is not resolved into *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate when repeatedly crystallised from light petroleum at the temperature of the laboratory. Potassium *l*-mandelate is completely racemised when heated with a large excess of potassium hydroxide in aqueous or ethyl-alcoholic solution.

28. "Certain Organic Phosphorus Compounds." By AUGUSTUS EDWARD DIXON.

In pursuing the study of the interaction of phosphorus halides with metallic thiocyanates (*Trans.*, 1901, lxxix., 541), the author has now succeeded in isolating phosphorus and phosphoryl "thiocyanates" respectively.

Phosphorus trithiocyanate, $\text{P}(\text{CNS})_3$, obtained from phosphorus trichloride and dry ammonium thiocyanate in presence of benzene, is an almost colourless oil boiling at 163° under 15 m.m. pressure, and having a sp. gr. 1.487 at 15.5° . When treated with water, a portion was quickly hydrolysed, forming phosphorous and thiocyanic acids; the remainder was hydrolysed exceedingly slowly, but otherwise no material difference in properties or composition was observed between this residue and a distillate not subjected to the action of water.

Phosphoryl trithiocyanate, $\text{PO}(\text{CNS})_3$, obtained from phosphorus oxychloride, is a clear, pale yellow, highly refractive oil, boiling at 175° under 21 m.m. pressure, and completely hydrolysed by cold water into phosphoric and thiocyanic acids, together with some isopenthiocyanic acid, resulting from the interaction of these products; it has a sp. gr. 1.520 at 13.5° .

These substances not only behave as thiocyanates, but also, to some extent, manifest the properties of thiocarbimides, being freely desulphurised by alkaline salts of lead and silver; they unite spontaneously with aniline, &c., fixing either one or three molecular proportions, according to the amount presented, to form amorphous solids, insoluble in cold water. The additive products are readily hydrolysed by contact with hot water, yielding in all cases approximately one molecular proportion of mono-substituted thiourea; a little hydrogen sulphide is evolved, but otherwise the rest of the contained sulphur appears as thiocyanic acid.

Certain tests which have been employed to distinguish between thiocyanates and thiocarbimides (such as treatment of the alcoholic solution with sodium, or the action of thiocetic acid) cannot be safely accepted as final where acylthiocyanates are concerned, all the latter so far examined being tautomeric in the sense that, under suitable conditions, they can behave as thiocarbimides to a greater or less extent if their power in this direction is measured by their capacity to fix aniline in the form of an immediate derivative of normal phenylthiocarbimide.

The study of these supposed tautomeric phenomena is being continued.

29. "Note on the Relation between the Chemical Composition of some Organic Substances and the Density of their Solutions." By CHARLES EDWARD FAWCETT.

The density of aqueous solutions of different salts in equivalent quantities is an additive property, and the principal relations are given by Valson's Law of Moduli. The relation of density in solutions of organic compounds (feeble electrolytes or non-electrolytes) to chemical composition or constitution is not yet so fully understood.

The author, in continuing an investigation on the amides (*Proc. Roy. Soc. Edin.*, 1904, xxv., 51), has measured the density of aqueous solutions of a number of amides at 25°, when the solutions contained the grm.-molecular weight of the substance dissolved in one litre. The densities of urea, methylurea, and *ns* dimethylurea solutions are 1.0155, 1.0137, and 1.0107 respectively; a comparison of these numbers with those obtained by Kanitz (*Zeit. Physik. Chem.*, 1897, xxii., 336) for ammonia, methylamine, and dimethylamine, namely, 0.9932, 0.9886, and 0.9856, shows that the differences for the corresponding numbers are fairly close to one another.

The densities of solutions of acetamide, propionamide, and butyramide are 1.0040, 1.0028, and 1.0006.

The values obtained for acetic, propionic, and butyric acids by Reyches (*Zeit. Physik. Chem.*, 1888, ii., 744) are 1.0084, 1.0066, and 1.0040, and show a similar relationship.

From these results, it will be seen that the density of such solutions is to a great extent an additive property, but constitution also plays some part, because isomeric substances give different values.

30. "The so-called 'Hydrocellulose.'" By ARTHUR LANDAUER STERN.

When cellulose is exposed to the action of dilute acids under certain conditions, the tenacity of the fibres is destroyed, and it falls to a powder which has been called hydrocellulose, and stated to have the empirical formula $C_{12}H_{20}O_{11}$.

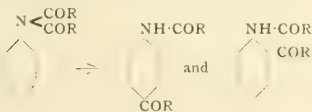
It is now shown that when the above reaction takes place, instead of a gain in weight, as theory indicates, there is invariably a loss, and that a small amount of soluble matter is formed, a portion of which, in all probability, is *d*-glucose.

The elementary composition of the powder is also shown to be identical with that of cellulose, the previous statements bearing on this point being founded on faulty experimental methods.

A hydrated cellulose is not formed under these conditions, but a hydrolysis takes place similar to that undergone by other carbohydrates under comparable conditions.

31. "Isomeric Change of Diacylanilides into Acylamino-ketones." By FREDERICK DANIEL CHATTAWAY.

When the diacylanilides are heated in presence of hydrogen chloride or zinc chloride, intramolecular re-arrangement takes place and the isomeric acylamino-ketones are produced thus:—



Such isomeric changes have been studied follow an exactly similar course to that of other analogous transformations in which atoms or groups of atoms pass from the nitrogen into an ortho- or para-position in the ring.

The introduction of a second acyl group into the nucleus has, however, not yet been effected (compare *Proc.*, 1902, xviii., 173; 1903, xix., 50, 57, 106, 124).

32. "Intramolecular Re-arrangement in Derivatives of the Aromatic Aminoketones." By FREDERICK DANIEL CHATTAWAY.

The acylchloroamino-derivatives of the aromatic ketones readily undergo the intramolecular re-arrangement characteristic of substituted aromatic chloroamines in which the halogen linked to the nitrogen changes place with a hydrogen atom attached to the ring in an ortho- or para position. The conditions necessary for the transformations to take place were indicated, and a series of new aromatic chloroaminoketones with their acyl derivatives was described.

Annual General Meeting.

The Annual General Meeting of the Society for the Election of Officers and other business will be held on Wednesday, March 23rd, at 5.30 p.m.

THE FARADAY SOCIETY.

Ordinary Meeting, February 2nd, 1904.

Dr. J. W. SWAN, F.R.S., President, in the Chair.

THE PRESIDENT referred in terms of deep sympathy to the recent lamented death of Mr. W. G. McMillan, and moved that resolutions giving expression to their sense of loss of a valued friend and colleague be sent to Mrs. McMillan and to the Council of the Institution of Electrical Engineers.

Mr. JONES read an abstract of a paper by Mr. S. O. COMPTON-COLES, entitled "Notes on the Welding of Aluminium."

The author commenced his paper by stating that soldered aluminium joints have proved unsatisfactory, as they will not stand the test of time, because galvanic action takes place between the aluminium and solder. One of the chief difficulties encountered other than the formation of oxide in soldering aluminium is, that a few degrees below its welding-point it passes into a pasty or brittle state, and being a very good conductor of heat, the solder very rapidly cools and freezes before it has time to flow sufficiently. He then proceeded to describe Dick's machine for welding aluminium by the removal of the oxide mechanically, combined with pressure. Reference was also made to Heraeus's process of welding aluminium, which consists in heating the aluminium in a reducing atmosphere until it reaches the pasty stage, when the joint is made by kneading and hammering. Emmé's process, which is somewhat similar, consists in heating the aluminium up to 600° C., and welding by hammering. The electric welding of aluminium has not proved commercially successful. A description was given of Schmidt's electric welding apparatus, which consists of a carbon stick, which is used in much the same way as a soldering iron, by being moved over the portion to be welded to remove the oxide, the aluminium forming one electrode, the carbon stick the other electrode. Jones's machine for welding aluminium tubes was also illustrated: a strip of aluminium is wrapped round a mandrel, and the joints are fixed together by passing a low tension current through the portions to be welded. The author then went on to describe his own process, which requires no flux or solder, and does not necessitate the hammering of the joint when in the pasty state, the process being especially suitable for wire, rods, and tubes. The machine employed is fitted with clamping screws which are controlled by levers. The aluminium is heated by a benzene lamp, and when raised to the point of fusion, pressure is applied to the levers, which causes the aluminium to be welded to unite, a ring of metal being squeezed out. This ring, which is largely composed of oxide, acts as an insulating and supporting collar, the molten metal being retained within it. Water is then projected on to the joint by turning a handle, at the same time a screen is moved in front of the flame. The rod is then removed, and when

the collar is filed off the joint will be found to be as strong as the rest of the metal. A table was given showing the tensile strength of twelve consecutive welds; in all the tests the specimen broke at some distance from the weld, and in no case did it actually break through the weld. Illustrations were given demonstrating how molten aluminium can be encased in a shell of aluminium oxide.

Mr. D. A. SUTHERLAND said the principle of the method was familiar to metallurgists who had to report on these matters. The great difficulty was where large pieces of aluminium had to be welded.

Mr. MURRAY MORRISON agreed with the last speaker; he himself had welded many joints in this way, although he did not quench. He always found that pressure was necessary. The chief novelty of the Cowper-Coles process lay in the apparatus.

Mr. BLOUNT said when drawn wires were welded it was essential that the joint be drawn or worked in some way, otherwise being cast metal it would be weaker than the rest of the wire.

Prof. HUNTINGTON thought that the chief novelty in the process lay in the fact that the metal was actually fused.

Mr. E. KILBURN SCOTT said that the important point to remember was the value of the hard outer skin of the metal. If aluminium wires were used for transmission of electricity, uniformity of section was unimportant, and the blob at the weld need not be removed. But otherwise, e.g., if used as trolley wires, it would be necessary to harden the joint in some way; this might be done by burnishing with agate. He showed by a diagram how a connection might be made without welding.

The PRESIDENT said that the apparatus they would shortly see at work showed a thorough appreciation of the conditions necessary to effect a weld, and in dealing with the film of oxide so as to hold together the molten metal made a virtue of a vice.

Mr. JONAS, in his reply, drew attention to the tests of tensile strengths of jointed rods given in the paper. In reply to Mr. Blount, the joints proved to be the strongest part of the rods. He would remark that the quenching was an essential feature of the process, and one which distinguished it from all others, the process being primarily a fusion process.

Dr. F. M. PERKIN then read an abstract of a paper by M. HOLLARD, entitled "Some Applications of the Theory of Electrolysis to the Separation of Metals from one Another." (See p. 110).

Mr. BLOUNT remarked that M. Hollard's method of preparing the cathode by throwing down on it the metal that is to be deposited, is one of extreme interest. The accuracy of the first method described was not sufficiently high for ordinary analytical purposes.

Dr. T. M. LOWRY, referring to the backward migration of the ions, said that as a rule this is much more strongly marked with a membrane than with a porous pot partition. Hittorf had recently been again working on this very subject.

Mr. G. WATSON GRAY read a short preliminary note describing an explosion of some high grade ferro-silicon which occurred spontaneously a short time ago at Liverpool.

The gases evolved on boiling a specimen in distilled water were found to contain PH_3 and AsH_3 . The former was in the greater proportion, and to that probably the explosions—which had created a considerable stir in Liverpool and which the author had not met with before—were due.

Mr. D. A. SUTHERLAND thought that the presence of only 0.1 per cent phosphorus made it very difficult to account for the explosions being due to phosphoretted hydrogen. It was essential to know the previous history of the metal.

Mr. R. H. HARLAND, who had gone into the matter, believed the explosion was due to calcium carbide, which had been previously made in the same furnace.

Mr. E. KILBURN SCOTT agreed with the last speaker; he had had a similar experience in making magnesite in furnaces that had been used for calcium carbide.

Mr. MURRAY MORRISON observed that all the ingredients necessary for CaC_2 are present in the manufacture of ferro-silicon.

Prof. HUNTINGTON said that ordinary ferro-manganese of over 80 per cent made in the blast-furnace disintegrates. This may be an action of the same kind; it is only a matter of degree.

The PRESIDENT said there was obviously a difference of opinion as regards the cause of these remarkable explosions; we must therefore wait the results of further inquiries, which he hoped would be presented to the Society, before we could be sure of the true explanation.

Mr. GRAY, in his reply, said there was certainly less than 0.1 per cent of calcium in this particular specimen of ferro-silicon. There was no doubt as to the presence of phosphoretted hydrogen in the gases evolved. He would report further in the matter, and Mr. Harland promised to do the same.

CORRESPONDENCE.

WHY ARE SOME ELEMENTS MORE ABUNDANT THAN OTHERS?

To the Editor of the Chemical News,

SIR,—In reply to my letter (CHEMICAL NEWS, vol. lxxxix., p. 47), Mr. Kingdon (CHEMICAL NEWS, vol. lxxxix., p. 58) suggests that the greater abundance of certain elements over others is only an apparent effect, because the heavier elements gravitate towards the centre of the earth and the lighter towards the surface; and that the centre of the earth is largely composed of heavy elements, such as gold and platinum.

In writing my former letter I had this possibility in mind (for which reason I wrote "a cause," not "the cause"), but I do not think that this "density" theory gives a full explanation of the facts.

In the first place, there is grave reason to doubt whether the interior of the earth is so very largely composed of very heavy elements. For example, the density of the earth is only 5.5, which is not great, compared with the surface density 2.7, when we consider the tremendous crushing pressure to which the matter in the interior is subjected.

Amagat compressed oxygen gas (3000 atmospheres) until it became denser than water.

Did the interior of the earth consist largely of gold and platinum the density of the earth would be very much greater than 5.5.

The density of the moon is still less than that of the earth; and other celestial bodies possess a still smaller density.

In the second place, there exist very puzzling anomalies as regards the distribution, which the "density" theory does not seem capable of explaining.

For example, why is chlorine (atomic weight 35.5) so much more abundant than F (atomic weight 19, Br (81), or I (126)? Why is argon (40) so much more abundant than neon (20), krypton (81), and xenon (128)? Why are O and Si (16 and 28) so much more abundant than N and P (14 and 32)?

The difference of density cannot account for these cases. Other causes of the different abundance of elements may be—

1. The greater rate of escape into space of the lighter elements, such as H and helium.
2. The different affinities of different elements for heavy metals, which leads to some being stored up in a combined form in greater quantities than others in the interior of the earth.

But even these causes do not account for the facts. For example, the argon group of elements do not unite with

elements, and all are volatile enough to occur in a gaseous form at the surface of the earth. Why then is argon the most abundant? It is neither the lightest nor the heaviest of this family of elements.

Again, bromine and iodine do not possess so great an affinity for other elements as does chlorine (which can displace them from their compounds), and so would not be any more likely than chlorine to be stored up in the interior of the earth.

Moreover, bromides and iodides are unstable under the action of heat—more so than the corresponding chlorides—and so would be even less capable of existing in the interior of the earth than chlorides.

In addition, the metallic iodides and bromides are more volatile and fusible than the corresponding chlorides (*cf.* AgI with AgBr, AgCl), and so would not be expected to occur in the interior of the earth in greater quantity than the chlorides on account of their greater involatility and fusibility.

Finally, the difference in volatility between Br, Cl, and I is so small, and the heat in the interior of the earth so great, that all would be expected to distil out more or less completely from the interior to the surface of the earth.

As a matter of fact, we are acquainted with matter which has come out from depths where the earth is white hot, and we find that Br and I are not more abundant in this matter than chlorine.

It is, in fact, indisputable that chlorine occurs throughout the earth's crust, from depths where it is white hot to the surface, in enormously greater quantities than Br or I.

For this reason I believe that chlorine is not only relatively, but also absolutely, more abundant than Br or I.

Precisely similar considerations apply to S and Se. The selenides are far more unstable under the action of heat than the sulphides. Se has a smaller affinity for metals and elements generally than sulphur, and so could not be expected to be stored up in greater quantities than sulphur at great depths.

Moreover, both elements are volatile enough to readily distil from the hot interior towards the surface of the earth.

Yet sulphur is a far more abundant element in every strata than selenium, even in volcanic lavas which have come out from depths where matter is white hot.

Indeed, I think that all the facts we know point to the conclusion that some elements occur in the universe in far greater quantities than others. Why?

Let us remember—

1. That heavy elements are less abundant than light elements.
2. That the phenomenon of radio-activity shows that heavy elements are less stable than light elements.

Are these two facts unconnected?—I am, &c.,

GEOFFREY MARTIN.

University of Kiel, January 31, 1904.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 5, February 1, 1904.

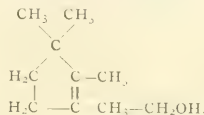
Action of Carbon on Quiklime at the Temperature of Fusing Platinum.—Henri Moissan.—The author finds that an intimate mixture of finely-powdered quiklime and sugar-carbon is not attacked when kept for ten minutes at the temperature of fusing platinum. No trace of calcium carbide can be found, and if the tube and its contents are placed in an inverted tube of water, not one bubble of acetylene can be detected even after several days.

Direct Reduction of Aromatic Halogen Derivatives by Finely-divided Nickel and Hydrogen.—Paul Sabatier and Alph. Mailhe.—The authors investigate the reaction taking place when reduced nickel in presence of hydrogen causes the direct reduction of the aromatic halogen derivatives without the addition of hydrogen to the radicle.

Manganous Salts as Oxydases in presence of a Colloid.—A. Trillat.—The author's experiments show that colloid solutions of manganese obtained in presence of albumin and an alkali possess very remarkable properties. During his researches on the physiological rôle of manganese, M. Bertrand put forward the hypothesis that proteid matter combined with this metal is in the most advantageous form for oxidising, and this opinion is confirmed by the author's results.

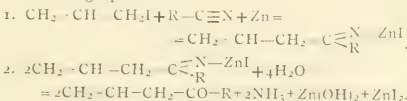
Mixtures of Antimony Trisulphide and Antimony.—H. Pellabon.—Antimony trisulphide and antimony, when intimately mixed and raised to a temperature above the fusing-point of antimony, do not usually give a homogeneous liquid, but two superposed liquids. The author investigates the causes of this phenomenon.

An Isomer of Borneol. Campholenic Alcohol and certain Campholenic Derivatives.—A. Béhal.—The author prepares campholenic alcohol, starting from inactive ethyl campholenate, and utilising MM. Bouveault and Blanc's method of reduction. He finds that the β -campholenol isomer of borneol has the constitution—



New Dinaphthopyranic Phenols.—R. Fosse.—The author discovers the curious property of pyranic phenols, which apparently belongs to the whole family, that they are insoluble in the aqueous alkalis and soluble in alcoholic alkalis. This anomaly of the phenolic function can be explained by admitting that the basicity of the pyranic oxygen neutralises the acidity of the phenolic hydroxyl to form a kind of salt stable in alkalis in solution in water; but, on the contrary, decomposable by alkalis in presence of alcohol. He also describes the new phenols which result from the copulation of dinaphthopyryl salts with the three ortho-, meta-, and para-cresols.

Alcoyl-allyl-ketones.—E. E. Blaise.—The author synthesises the alcoyl-allyl-ketones by condensation of allyl iodide with the nitriles in the presence of zinc. The condensation should be effected at 0° and contact prolonged for about twenty-four hours. The reaction is expressed by the following equations:—



Oxalcoyl-ethylenic Carbides and Acids.—Charles Moureu.—The author isolates in a pure state a series of oxalcoyl-ethylenic acids, $\text{RC}(\text{OR}')=\text{CH}-\text{CO}_2\text{H}$, and oxalcoyl-ethylenic carbides, $\text{RC}(\text{OR}')=\text{CH}_2$, and investigates the various decompositions of these compounds. Further, he condenses certain alcohols with phenyl-acetylene.

Reduction of Nitrobenzoic Acetals and Acids.—P. Freundler.—An investigation of the reduction of *o*-nitrobenzoic alcohol and the ether oxides has shown the influence of the substitutions of the radicle on the formation of azoics. The author completes the researches by submitting to the same treatment (powdered zinc, alcohol, and soda) the three acetals and *o*- and *p*-nitrobenzoic acids.

MISCELLANEOUS.

Forthcoming Book.—Messrs. Crosby Lockwood and Son announce for early publication a treatise on "The Oil Fields of Russia and the Russian Petroleum Industry," by A. B. Thompson, A.M.I.M.E. Mr. Thompson, as Chief Engineer and Manager for some years in Russia of one of the leading English companies, has had very wide and exceptional experience in the exploration, exploitation, and management of oil-bearing properties. Besides dealing with these subjects, he has added to the work Notes on the Origin of Petroleum in Russia, and a translation of the Imperial Rules and Regulations concerning Oil Properties. The work is very fully illustrated with diagrams, photographic plates, and maps.

Presence of Formic Aldehyde in Atmospheric Air.—H. Henriet.—The author discovers traces of formic aldehyde in the air. This body is a powerful antiseptic, and therefore plays an important part in the purification of the air. It is an important factor in public hygiene, in addition to its action in vegetable physiology. He estimates the formaldehyde in the air by passing the latter, after filtration, over red mercury oxide heated to 250° and comparing the carbon dioxide thus obtained with that normally existing in the air. He finds the quantity varies between 1/100,000 and 5/100,000 of the weight of the air, and is proportional to the exterior temperature.—*Comptes Rendus*, cxxxviii., No. 4.

Organo-mercuric Compounds of Salicylic Acid.—G. Buroni.—The basic salicylate of mercury, to which up till now the formula $C_6H_4<\overset{O}{\underset{CO_2}{>}}Hg$ has been given, should, on the contrary, be looked upon as a compound containing a nuclear atom of mercury; that is $C_6H_3<\overset{OH}{\underset{CO_2}{>}}Hg>O$ in every respect analogous to Peschi's mercurio-benzoic anhydride. *Oxymercuriosalicylic anhydride*.—This body can be obtained by the known methods, or by boiling a molecule of salicylic acid with 1 molecule of acetate of mercury; the precipitate is dissolved in dilute soda and re-precipitated with CO_2 . It is a white powder, decomposing when heated. The ammonium salt occurs in easily decomposable needles, soluble in water. *Chloro-mercuriosalicylic acid*, $C_6H_3<\overset{OH}{\underset{CO_2}{>}}HgCl$, occurs in needles, soluble in boiling alcohol. It is obtained by the action of acetic acid on the salts. *Bromomercuriosalicylic acid* is prepared in the same manner as the preceding ones.—*Gazz. Chim. Ital.*, vol. xxxii., p. 305.

Problem of the Systematic Classification of Inorganic Compounds.—M. Locke.—We know that Abegg and Bödlander look upon the properties of the organic salts as functions of the electro-affinity of the ions in solution (*Zeit. Anorg. Chem.*, vol. xx., p. 453). In a previous paper the author has arrived at results contrary to the views expressed by these chemists (*Ann. Chem. Journ.*, vol. xxvii., p. 105). In the case of monovalent metals, a compound is the more soluble as it has less tendency to form complex salts. The more easily it forms ammoniacal compounds, the greater tendency it has to form double salts, and the less easily it is soluble. However, the thallous salts form an exception, for the halogenides, though slightly soluble like the salts of silver, do not form complex ions, thus behaving like the salts of sodium. If we consider the elements of different valencies, the relations which exist between the solubility and facility to form double salts and ammoniacal derivatives are not necessarily in the same sense. Thus with zinc the formation of complex ions seems to be connected with the great solubility of the salts. The author then proceeds to deal with the relations existing between the solubilities of compounds and

the place of the elements in the periodic system. In the chloride, bromide, iodide system, for example, the solubility increases from the chloride to the iodide if the chloride is easily soluble (Na, Ba, K, Fe). If, on the other hand, the chloride is not easily soluble, the solubility of the iodide is almost nil (Ag, Pb, Tl, Hg). In the latter portion of this paper the author deals with the solubility of the alums and the sulphates of the magnesium series:—

Solubility of the Alums in Grm.-molecules per Litre.

	Al.	Cr.	Va.	Fe.
Cs	0.013	0.015	0.020	0.045
Rb	0.059	0.078	0.177	0.293
Tl	0.177	0.212	0.573	0.799
NH ₄	0.387	0.407	1.210	1.659

With the alums the influence of an element on the solubility of the isomorphous mixtures may be represented by a constant which remains the same for the whole series of alums.—*Zeit. Anorg. Chem.*, vol. xxxiii., p. 58.

MEETINGS FOR THE WEEK.

- MONDAY, 7th.—Society of Arts, 8. (Cantor Lectures). "Recent Advances in Electro-chemistry," by Bertram Blount, F.I.C.
 --- Royal Institution, 5. General Monthly Meeting.
 --- Society of Chemical Industry, 8. Presentation to Mr. A. R. Ling. "Observations on Cotton and Nitrated Cotton," by H. de Moshenthal. "The Products, and Relative Temperature of Combustion of some Smokeless Powders," by W. Macnab and A. K. Leighton.
 TUESDAY, 8th.—Royal Institution, 5. "Japanese Life and Character," by Ernest Foxwell, M.A.
 WEDNESDAY, 9th.—Society of Arts, 8. "Mechanical Piano Players," by J. W. Coward.
 THURSDAY, 10th.—Royal Institution, 5. "Electrical Methods of Measuring Temperature," by Prof. H. L. Callendar, F.R.S.
 --- Society of Arts, 4.30. "China Grass—its Past, Present, and Future," by Frank Birdwood, B.A.
 FRIDAY, 11th.—Royal Institution, 9. "The Motion of Viscous Substances," by Prof. Frederick T. Trouton, F.R.S.
 --- Physical, 8. (At Royal College of Science, South Kensington). "The Whirling and Transverse Vibrations of Shafts," by Dr. C. Chree, F.R.S. "Notes on Non-homocentric Pencils, and the Shadows produced by them—Part II, Shadows produced by Axially Symmetrical Pencils possessing Spherical Aberration," by W. Bennett. Exhibition of Apparatus by Messrs. Pye and Co., Cambridge.
 SATURDAY, 12th.—Royal Institution, 3. "The Life and Work of Stokes," by Right Hon. Lord Rayleigh, F.R.S.

The following Reminders of Stock are to be sold far below value:—

VALERAN ACID.
 V-LEKIAN OIL AND ETHER.
 RUM ETHER. BUTTER ETHER.
 FORMIC ETHER. FORMIC ACID.
 SUBSTITUTE OF LINSEED OIL.

C. D. RAMM, Hamburg 8, Germany.

M I C A .

Telephone
No. 2248
Avenue.

WIGGINS & SONS, 10, Tower Hill, E.C., & London
 102 & 103, MINORIES, E.C.,
 MICA Merchants.
 Manufacturers of Mica Goods or Electrical and ALL purposes
 Contractors to His Majesty's Government

E. GEORGE & SONS,
 BOOK-SELLERS.

161, WHITECHAPEL ROAD, LONDON, E.

Are OPEN TO PURCHASE Complete Sets
 or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.
 Current Catalogue of General Literature sent on application

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2311.

THE ELEMENTS: VERIFIED AND UNVERIFIED.*

By CHARLES BASKERVILLE, Ph.D., F.C.S.,
Smith Professor of General Chemistry, University of North Carolina.

(Continued from p. 110.)

THE imposition upon your good nature practised in the foregoing craves its pardon in an effort to seek a definition for the term *element*. Shall we say, as does Remsen, "an element is a substance made up of atoms of the same kind?" Can we say that it is not? Venable truly says ("Definition of the Element," *loc. cit.*): "An element is best defined by means of its properties." These conceits are not exclusive. The properties are the result of the action of physical forces and chemical affinity, whatever that may be. Certain of the novel atmospheric gases have so far responded but poorly to the latter, as predicted before their discovery by Flawitzky, Julius Thomsen, and de Boisbaudran in 1887. This necessitates, according to Piccini, our dividing them at once into two classes (*Zeit. Anorg. Chem.*, 1899, xix., 295).

Pattison Muir gives a satisfactory definition ("The Alchemical Essence and the Chemical Element," London, 1894):—"The notion of the elements that has been attained after long continued labour is that of certain distinct kinds of matter, each of which has properties that distinguish it from every other kind of matter, no one of which has been separated into portions unlike the original substance, and which combine together to produce new kinds of matter that are called compounds." The following simpler definition has finally served as my guide:—*An element is that which has not been decomposed, so far as we are aware, into any thing other than itself.* In short, it is consistent.

It is well to stop occasionally and take stock. The Daltonian centenary could not but be an opportune time. Stable certified securities are not enumerated in the list which follows. Having in mind the second chapter of the first book of Chronicles, certain so-called elements are mentioned; for yttrium begat cerium, and cerium begat lanthanum, and lanthanum begat samarium and didymium, and didymium begat neodidymium and praseodidymium, and praseodidymium begat α - and β -praseodidymium, "and so weiter."

Unpractised as a reading clerk, I shall spare you the strain of hearing this long list of elements on probation, but submit for leisure perusal printed copies.

From the table have been omitted urstoff, protyle (Crookes), electrons (Lodge), corpuscles (J. J. Thomsen), and pantogen (Hinrichs). It appeared also unnecessary to incorporate phlogiston, nitricum (the imaginary body, thought by Berzelius united with oxygen to form nitrogen), and *aræon* (ponderable caloric). According to Meissner, hydrochloric acid is composed of two equivalents of oxygen, one of water, combined with *aræon*, and the imaginary radical *murium* (*vide* Bolton). Often alloys have been prepared and given names like the elements, "magnalium" for example. These are omitted also. Otherwise, I have purposely included every suggestion of an element I could obtain. The summary, while doubtless deficient, may secure an historical vindication.

What shall we do with these numerous aspirants whose recognition is urged? "These elements perplex us in our

researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us, mocking, mystifying, and murmuring strange revelations and possibilities," said Crookes referring to the rare earths. Some have been verified, many unverified; some are true, some are false. Without doubt some have been presented without sufficient stage setting, yet the good faith of many can not be questioned. In fact, from this list, as one reads, he perceives the whole gamut of scientific emotions. There he may find the tragedies of elemental pretension, the comedies, yea, the very farces.

We need not look far to ascertain explanations for certain incorrect conclusions. The extreme rarity of the minerals in which many of the tentative elements have been detected, the excessively small percentages of the new ingredients, and the extraordinary difficulties attending their separation from known and unknown substances, combine to render the investigations laborious, protracted, and costly. De Boisbaudran required 2400 kilograms of zinc blende for 62 grms. of gallium. Ramsay (*Zeit. Phys. Chem.*, 1903, xlv., 74) has shown one part of krypton in twenty million volumes of air, while a like amount of xenon requires one hundred and seventy million. How patiently and persistently that modest Parisian couple followed Becquerel's rays!

Furthermore, when one feels that he has obtained something novel, the absolute proof is fraught with difficulties and uncertainties. We have decided to define an element by its properties. The alterations produced in the properties of the most characteristic elements by the presence of small amounts of foreign substances are evident in steel. The influence of arsenic upon the conductivity of copper is well known, and Le Bon (*Comptes Rendus*, 1900, cxxxi., 706) has recently shown that traces of magnesium (one part in 14,000) in mercury cause the latter to decompose water and to oxidise rapidly in the air at ordinary temperatures. Thorium with less than a trace of actinium produces an auto-photograph.

This point can not be too strongly stressed in the rare earth field. One who has wrought with thorium dioxide well knows the influence a small amount of cerium has upon its solubility. The conflicting statements in the literature as to the colours of the oxides of the complexes, neodidymium and praseodidymium, cause one to wonder if different researchers have had the same hæccecya.

An appeal to the spectroscope is of course in the minds of all my hearers.

It was once supposed that each element has its characteristic spectrum which remained the same under all circumstances. Keeler calls attention to modern investigations which have shown that the same element can have entirely different spectra (*Scientific American Supplement*, 1894, lxxviii., 977, and *Popular Astronomy*). For example, oxygen may be caused to have five different spectra, nitrogen two, &c. In fact, there is no indication in the appearance of the spectra that they belong to the same substance; yet through the result of the work of Rydberg, Kayser, Runge and Precht, series of groups of lines are had which satisfy mathematical formulæ.

"It was proposed by de Gramont, at the International Congress in Paris, in 1900, and agreed, that no new substance should be described as an element until its spark spectrum had been measured and shown to be different from that of every other known form of matter."

As Hartley remarks (Address before the Chemical Section of the British Association, Southport, 1903):—"This appears to me to have been one of the most important transactions of the Congress." Radium was the first to be tested by this rule (Runge and Precht, *Ann. Physik.*, 1903, [4], xii., 407). Exner and Haschek obtained 1193 spark and 257 arc lines for Demarcay's europium. It must not be forgotten, however, that, by overlapping, lines in mixtures may be masked or appear, which are absent in those bodies of the highest state of purity. It must not be forgotten that pressure influences the spectrum, usually producing a broadening of the lines, as shown by Schuster ("British Association Report," 1880, 275; *vide* also

* Address of the Vice-President of Section C (Chemistry) of the American Association for the Advancement of Science, St. Louis Meeting, December 28, 1903.

Lockyer and Frankland, *Proc. Roy. Soc.*, 1869, xxvii., 288), and that it may occur symmetrically or only towards the least refrangible red. Lest we forget, the spectroscope failed a long time to show radium, and we knew it was there. It must not be forgotten, as G. Krüss has shown, that the "influence of temperature cannot be neglected and ignored, but must be considered by every chemist who wishes to make correct spectroscopic observations" ("The Influence of Temperature upon the Spectrum—Analytical Observations and Measurements," *Liebig's Annalen*, cccxxviii., 57; *CHEMICAL NEWS*, lvi., 51). It is well known to spectroscopists that band spectra are obtained at temperatures intermediate between those required for the production of continuous spectra and line spectra ("Spectrum Analysis," Landauer, English translation by Tingle, p. 70). The explanations of these facts do not concern us at present.

It has been shown by the researches of Newton, Dale, Gladstone, Jamin, Schrauff, Landolt, and others that the refractive power increases in all liquids, except in water, between 0° and 4° with the increase of density—that is, with decrease of temperature. Rydberg showed that various solid bodies, such as quartz and aragonite, follow the same law. There are some exceptions, however. Among these is glass, as proved by Arago and Neumann prior to Rydberg. "On a rise of temperature, all phenomena of absorption or emission are displaced toward the violet with the glass prisms, but toward the red with quartz prisms. These displacements are the greater the more refrangible the region of the spectrum in which they occur." As a result of a large number of observations, Krüss learned that by a variation of 25°, marked changes would be observed in the spectroscopic lines. From a table given, it could be seen that errors may spring from neglect of the temperature (of the instrument?) in stating wave-lengths, since a rise of 5° is sufficient to transfer the D₂ to the position D₁. Roscoe obtained an entirely new spectrum with the metal sodium, whereby it appears that this metal exists in a gaseous state in four different degrees of aggregation, as a simple molecule, and as three or four or eight molecules together.

Grünwald ("Über das Wasserspectrum, das Hydrogen und Oxygenspectrum," *Phil. Mag.*, 1887, xxiv., 304; "Math. Spectralanalyse des Magnesiums und der Kohle," *Monatshefte für Chemie*, viii., 650; "Math. Spectralanalyse des Kadmiums," *Monatshefte für Chemie*, ix., 956) in a series of papers on his theory of spectrum analysis endeavours "to discover relations between the spectra and thus to arrive at simpler, if not fundamental, 'elements.'" He came to the conclusion that "all the so-called elements are compounds of the primary elements *a* and *b*" (coronium and helium). Ames (*Am. Chem. Journ.*, 1889, xi., 138), having called attention to the use of uncorrected data by Grünwald, remarks:—"The concave grating gives the only accurate method of determining the ultra-violet wave-lengths of the elements, and as a consequence of not using it, most of the tables of wave-lengths so far published are not of much value."

Hutchins and Holden, after a comparative study of the arc spectra of metals and the sun with a twenty-one-foot focal Rowland grating, state ("On the Existence of Certain Elements, Together with the Discovery of Platinum in the Sun," *Am. Journ. Sci. & Sci. Am. Supp.*, 1888, xxv., 628):—"We are convinced that there is much in the whole matter of coincidences of metallic and solar lines that needs re-examination; that something more than the mere coincidence of two or three lines out of many is necessary to establish even the probability of the presence of a metal in the sun. With the best instruments the violet portion of the solar spectrum is found to be so thickly set with fine lines that, if a metallic line were projected upon it at random, in many places the chances for a coincidence would be even, and coincidences could not fail to occur in case of such metals as cerium and vanadium, which give hundreds of lines in the arc."

"Moreover, a high dispersion shows that very few lines

of metals are simple and short, but, on the contrary, winged and nebulous, and complicated by a great variety of reversal phenomena. A 'line' is sometimes half an inch wide on the photographic plate, or it may be split into ten by reversals."

Lockyer maintained that the lines of certain substances vary not only in length and in number, but also in brilliancy and in breadth, depending upon the quantity of the substance as well as temperature (*Roy. Soc. Proc.*, lxi., 148, 183; *CHEMICAL NEWS*, lxxix., 145). Being unable to decompose the elements in the laboratory, he studied the spectra of the stars. The spectra of the colder stars (*CHEMICAL NEWS*, lxxix., 147) show many more metals but no metalloids, whereas the coldest stars, *α Orionis*, show the Crookes spectrum of metalloids which are compounds. None of the metalloids are found in the spectrum of the sun. Over 100,000 visual observations and 2000 photographs were made in the researches.

Livinge (Address before the Chemical Section of the British Association; *Scientific American Supplement*, 1882, xiv., 356), as the result of the work of Young, Dewar, Fievez, and himself on the spectrum of the sun, by which some lines were resolved with a new instrument, which they before had not been able to devise, comments on Lockyer's work. That the coincidence of rays emitted by different chemical elements, especially when developed in the spark of a powerful induction coil, and the high temperature of the sun and stars, gives evidence of a common element in the composition of the metals which produce the coincident rays. "This result cannot fail to shake our belief, if we had any, in the existence of any common constituent in the chemical elements, but it does not touch the evidence which the spectroscope affords us that many of our elements, in the state in which we know them, may have a very complex molecular structure."

Hartley (*loc. cit.*) in his recent admirable address said:—I have always experienced great difficulty in accepting the view that because the spectrum of an element contained a line or lines in it which were coincident with a line or lines in another element, it was evidence of the dissociation of the elements into simpler forms of matter. In my opinion evidence of the compound nature of the elements has never been obtained from the coincidence of a line or lines exclusively belonging to the spectrum of one element with a line or lines in the spectrum exclusively belonging to another element. This view is based upon the following grounds:—(1) Because the coincidences have generally been shown to be only apparent, and have never been proved to be real; (2) because the great difficulty of obtaining one kind of matter entirely free from every other kind of matter is so great that where coincident lines occur in the spectra of what have been believed to be elementary substances, they have been shown from time to time to be caused by traces of foreign matter, such as by chemists are commonly termed impurities; (3) no instance has ever been recorded of any homologous group of lines belonging to one element occurring in the spectrum of another, except and alone where the one has been shown to constitute an impurity in the other; as, for instance, where the triplet of zinc is found in cadmium and the triplet of cadmium in zinc; the three strongest lines in the quintuple group of magnesium is graphite, and so on. The latest elucidation of the cause of coincidences of this kind arises out of a tabulated record from the wave-length measurements of about three thousand lines in the spectra of sixteen elements made by Adeney and myself. The instances where lines appeared to coincide were extremely rare; but there was one remarkable case of a group of lines in the spectrum of copper which appeared to be common to tellurium; also lines in indium, tin, antimony, and bismuth, which seemed to have an origin in common with those of tellurium.

The last sentence presents the point I wish to emphasise. Tellurium has long obtruded itself before a satisfactory vision of the natural system. The table appended alone recites not a few efforts to obtain the contaminating

constituent of tellurium which *a priori* is present from Hartley's observations (see also Grünwald, 1889, table). The fractionation of a rubidium-caesium mixture, perhaps, is a simpler problem than that confronting Pellini (*Gazz. Chim. Ital.*, xxxiii., 11, 35), who reports a definite amount of an element with a high atomic weight (about 214) similar to, and associated with, tellurium.

What has been said especially to the elements of the rare earth class—"asteroids of the terrestrial family"—as phrased by Crookes. Many of them have not been secured with sufficient purity to claim an inherent spectrum; further, the spectra attributed have not been obtained under uniform conditions.

To be continued.

ON THE LAW OF THERMIC CONSTANTS, AND THE HEAT OF FORMATION OF COMPOUNDS OF BARIUM.

By D. TOMMASEI.

M. GUNTZ has recently determined the heat of oxidation of barium (*Comptes Rendus*, May 4, 1903), and found $\text{Ba} + \text{O} = \text{BaO}$ solid, 133.4 cal. This figure enables us easily to calculate the actual heat of formation of dissolved chloride of barium, which is equal to 198.8 cal.

To obtain the thermic constant of barium it suffices to subtract from the heat of formation of dissolved chloride of potassium the heat of formation of the chloride of barium, also dissolved: $2 \times 100.8^* - 198.8 = 2.8$ cal. Knowing the thermic constant of barium (2.8 cal.), it is easy to determine, with the help of the law of thermic constants, the heat of formation of all the soluble compounds of this metal. (For further details see *Bull. Soc. Chim.*, 1883, pp. 384, 390, and 602; and the "Traité d'Electrochimie," by D. Tommasei, p. 850).

Heats of Formation of the Compounds of Barium.

	Calculated	1 pound
	Calories.	Calories.
Bromide of barium	179.2	179.2
Iodide	146.6	146.6
Nitrate	189.4	189.2
Perchlorate	190.0	190.4
Chlorate	189.2	189.0
Hydrate	191.8	191.4
Formate	188.6	188.4
Acetate	188.4	188.2
Ethylsulphate of barium ..	189.2	189.2
Glycolate	189.2	189.2
Benzinosulphate	188.6	188.8
Picrate	188.6	189.0

The following are the heats of formation of some compounds of barium which have not yet been determined experimentally, but which can be calculated by the law of thermic constants. This law, which I discovered in the year 1882, may be stated as follows:—When a metal is substituted for another in a saline solution, the heat given off by each metal is always the same, no matter what may be the nature of the acid radical present in the salt.

Compounds.	Calories.
Bichromate of barium	188.6
Butyrate	139.0
Chloracetate	190.4
Trichloracetate	189.8
Amidobenzoate	180.2
Nitrobenzoate	187.2
Benzoate	188.6
Lactate	188.6

* The heat of formation of chloride of potassium determined by Thomson.

Thus we see that, by knowing the heat of formation of a single compound of barium, it is possible, thanks to the law of thermic constants, to determine with the greatest accuracy the heats of formation of all the other soluble compounds of barium.

It is very evident that what I have just stated for compounds of barium can be applied, without exception, to all the soluble mineral and organic salts.—*Bull. Soc. Chim.*, Series 3, xxix., No. 16.

THE CHEMICAL ANALYSIS OF TWO RARE MINERALS FROM THE CAUCASUS. IN THE BATOUM DISTRICT.

By G. P. TCHERNIK.

THE author has explored the delta of the river Tchorokh, and has collected several minerals from the country traversed by this river or its affluents. The complete analysis of two rare minerals is given below. They were found in a rock of granitic nature, formed of felspar of a light colour in fairly large crystals, with large white flakes of mica, and dark coloured quartz—a mixture in which the felspar is predominant.

One of these minerals occurs in plates of 2 to 2.5 m.m. thick, separated one from the other by thin layers of brown oxide of iron. Their structure is crystalline, though their form has not been determined; their lustre is greasy, hardness = 5.5, density = 5.485; their colour is velvet-black; and their fracture conchoidal. When heated, they split up, become opaque, and take a brown colour; after heating strongly, their density diminishes by about 5 per cent; in the blowpipe flame, they fuse on the edges with difficulty, and give a dark greyish coloured glass. The borax bead is dirty red in the oxidising flame, and dark green in the reducing flame; the phosphorus-salt bead is greenish in both flames. The analysis has been made minutely, and is as follows:—

	Per cent.
Ta ₂ O ₅	26.88
Nb ₂ O ₅	33.80
Y ₂ O ₃	6.15
Er ₂ O ₃	4.22
Ce ₂ O ₃	3.82
La ₂ O ₃	1.07
Di ₂ O ₃	0.74
ThO ₂	3.23
ZrO ₂	4.17
U ₂ O ₃	4.37
FeO	7.36
MnO	traces
CaO	0.94
TiO ₂	0.60
TeO ₃	1.90
SnO ₂	traces
MgO	traces
K ₂ O	0.48
Na ₂ O	0.80
Al ₂ O ₃	0.25
SiO ₂	0.22
	99.00

A comparison with the analyses of analogous minerals points to a variety of samarskite.

The second of these minerals occurs in short prisms, badly formed and striated in some places; their colour is steel-grey, with a metallic lustre, more or less tarnished in some parts; it is opaque in the mass, but is translucent at the edges; the fracture is irregular, the hardness 6, and density 5.365; their composition is much less complex than that of the preceding one. The results of the analysis are:—

	Per cent.
Nb ₂ O ₅	62.80
Ta ₂ O ₅	19.72
FeO	11.16
MnO	2.85
TeO ₃	0.14
SnO ₂	0.60
ZrO ₂	0.54
SiO ₂	traces
Al ₂ O ₃	traces
	97.81

This mineral appears to be a variety of columbite or niobite.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 684.

CONSTANT-STANDARD SILVER TRIAL-PLATES.*

By EDWARD MATTHEY,
C.B., F.S.A., F.C.S., Assoc. Roy. Sch. Mines.

REFERRING to my paper communicated to the Royal Society, February 16, 1894, and read March 15, 1894 (*Proc. Roy. Soc.*, 1894, lv., p. 265), in which it was shown that moderately sized plates of sterling silver of a uniform

Weighing 6.655 kilograms.

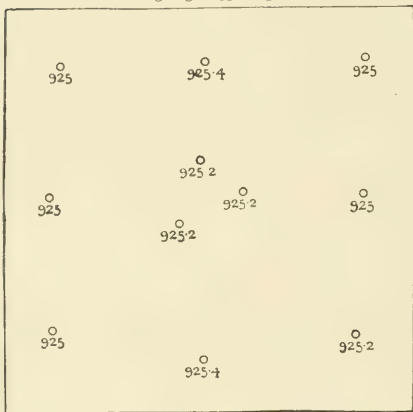


FIG. 1.

Both 75 c.m. by 75 c.m. and 1 m.m. in thickness.

states:—"From the foregoing remarks it will be evident that it is impossible to cast a standard silver plate or bar of uniform composition, and it was necessary therefore to resort to an artifice in order to obtain a standard trial-plate of the required dimensions." ("Fourth Annual Report," Deputy Master of Mint, 1873, pp. 44-46.)

The means adopted by him were to cast 1000 ozs. of standard silver into a skillet-mould 30 c.m. long, 25 c.m. wide, and 5 c.m. broad, to plane off 4 m.m. from its surface, and to roll the planed skillet to 1.8 m.m. thickness, a sheet being produced 1.5 m. long, 45 cm. wide. From this the portion was cut which showed constant results about 925, but which varied from 924.6-925.1; and the rest of the plate, which varied from 924 (lowest) to 928.4 (highest), was abandoned. He shows all these results by diagrams accompanying his memoranda. The portion of available constant standard so cut out from the 1000 oz. sheet weighed 104 ozs., about one-tenth of the whole plate. And this 104 ozs. (= 3.230 kilograms.) formed the mint trial plate from a mass of 1000 ozs. (= 31.103 kilograms.) specially cast for the purpose.

Notwithstanding that many experiments were subsequently made by Prof. Roberts-Austen to find a means of obtaining a constant standard trial-plate, in 1899 he was compelled to resort to what he calls the "cumbersome expedient" of 1873. His statement is:—"None of the

Weighing 6.624 kilograms.

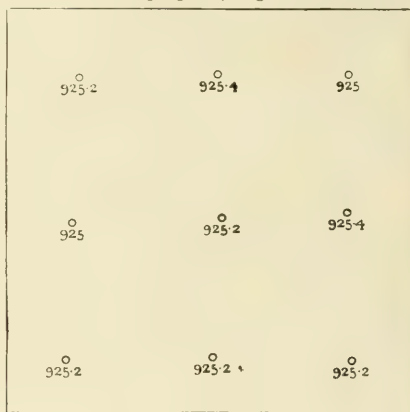


FIG. 2.

standard could be obtained by casting from thin castings, my attention since then was drawn to the difficulty of casting larger quantities than those described in that paper, which were only of an average weight of 4 to 5 kilograms per plate, and to the desirability of obtaining a large plate, say of some 8 or 10 kilograms, in weight without difficulty, and I have therefore resumed my attention towards effecting this. It appears that considerable difficulties have been experienced with regard to obtaining large plates of constant standard.

In the Royal Mint Report of 1873 is a memorandum appended by Prof. W. Chandler Roberts, which refers to a series of well-known experiments with regard to obtaining a constant alloy of 0.900 silver by Leval in the Paris Mint, he himself being at the time engaged in the preparation of a standard silver trial-plate. Prof. Chandler Roberts

results were satisfactory, and eventually, after no less than 31 plates had been cast without success, recourse was had to the method adopted in 1873, of casting a large mass of metal and detaching a particular portion, which proved by assay to be of approximately uniform standard." ("Thirtieth Annual Report," Deputy Master of Mint, 1899, pp. 69, 70.)

The casting of the standard silver into thin instead of into the thick moulds ordinarily employed having been attended with such excellent results (*vide* my paper of February 16, 1894, before referred to), I was induced to believe that it must be due to the more rapid cooling of the metal by which liquation was arrested; so that if the standard silver were cast into moulds sufficiently cooled, liquation might be induced to disappear altogether. In order then to overcome the difficulty of obtaining the standard trial-plates in larger sizes, I commenced by casting quantities of not less than 8 kilograms. into a mould cooled externally by ice, and also by freezing mixtures as

* A Paper read before the Royal Society, February 11, 1904.

low as 10° C., and by these means I obtained most encouraging results—results which confirmed me in the supposition that by cooling with rapidity there is less time for liquation, which appears to be the direct converse of what has been supposed hitherto, viz.: “that a uniformity of standard was best attained by slow and uniform cooling” (*vide* memorandum already referred to in Mint Report, 1873). But although I thus obtained exceedingly good

Another cast simply into a cold mould, and rolled to a thickness of 1 m.m., gave the results shown in Fig. 5.

This only weighed 3.640 kilograms., is without any wave of variation, and is absolutely constant.

The hitherto accepted theory “that the molecular rearrangement is comparatively slight if the mass of metal is slowly and uniformly solidified” (“Fourth Annual Report,” Deputy Master of Mint, 1873, p. 46) is contradicted by

Weighing 7.870 kilograms.

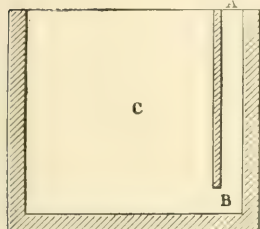


FIG. 3.—Rough Section of Cast-iron Mould employed.

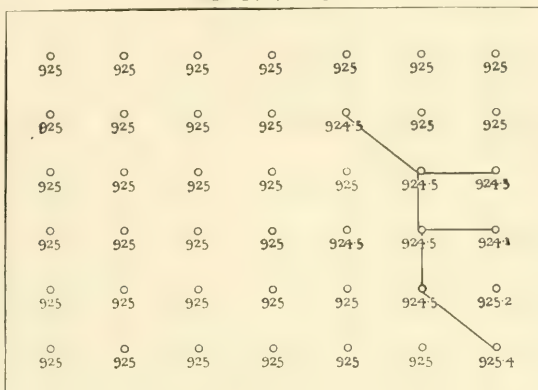


FIG. 4.

75 c.m. by 90 c.m. and 1 m.m. in thickness.

results (Figs. 1 and 2) I was not satisfied that this was the best way of producing a constant-standard plate.

I therefore adopted a different method of casting the standard silver. Instead of pouring the melted alloy into a mould from the top, I poured it into a mould by which the skillet was produced from the bottom (see Fig. 3).

By pouring the alloy into the gate A, the metal passes by B into the space C. And instead of cooling the mould

the results I have obtained; and the results all bear out the fact that there is little or no difficulty in obtaining an 8 or 10-kilogram. plate of constant-standard silver, or even more if necessary.

SOME APPLICATIONS OF THE THEORY OF ELECTROLYSIS TO THE SEPARATION OF METALS FROM ONE ANOTHER.*

By A. HOLLARD.

(Concluded from p. 113).

II. Influence of the Nature of the Cathode.

By suitably choosing the metal for the cathode, it is possible to avoid completely the liberation of hydrogen, even in strongly acid solution, and thus to increase sufficiently the conductivity of the bath so that the separation of the metals becomes possible. Moreover, if the metal of the cathode raises the polarising E.M.F. of hydrogen above the polarising E.M.F. of the metal M it is proposed to deposit, at the same time keeping it below the polarising E.M.F.'s of the metals which are to remain in the bath, it becomes impossible, as a rule, for these metals to be deposited. In fact, if one does reach the E.M.F. at which they are deposited, this potential, being higher than that of hydrogen, causes in acid solution a sufficiently abundant evolution of gas to prevent their deposit. If evolution of hydrogen occurs, it shows that the E.M.F. being used is too great.

The above requires amplifying a little.

Let us call to mind first that in electrolytic analysis the metals are divided into two principal classes, according as

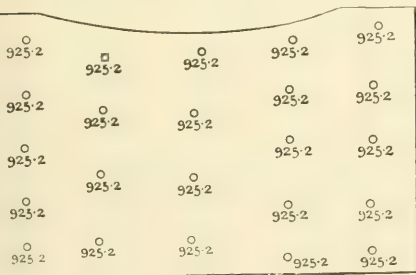


FIG. 5.

by ice or freezing mixture I used the mould simply cold. I have obtained excellent results by this method. Subjoined is one of the plates produced rolled to 1 m.m. thick, measuring 90 c.m. $\times$ 75 c.m. and weighing 8.700 kilograms. Trimming the rough edges from the plate about 1 c.m., the results came out as under, showing a constancy of 925 nearly all over the plate. I have drawn a line where the only wave of lower variation occurs (Fig. 4).

they are or are not capable of being deposited on the cathode in strongly acid solution.

The metals which cannot deposit themselves in strongly acid solutions are those which, in order to cover the cathode, require potentials higher than that at which hydrogen begins to evolve; one sees then that, under the influence of these high tensions, a strongly acid solution—that is, one containing a large proportion of H^+ ions—gives rise to such an abundant evolution of hydrogen at the cathode, that all precipitation of metal there becomes impossible. On the other hand, metals which can be deposited on the cathode in strongly acid solution are those which require for this precipitation potentials lower than the polarisation potential of hydrogen; their deposition is not then interfered with by hydrogen.

If we call the polarisation potential of hydrogen zero, we shall have the following values for the polarisation potentials of the principal metals (Nernst and Wilsmore, *Zeit. f. Elektrochem.*, November 8, 1900):—

TABLE I.

Metals which cannot be Deposited in Strongly Acid Solution.

Zn..	..	..	..	+0.77
Cd..	..	..	..	+0.42
Fe..	..	..	..	+0.34
Co..	..	..	..	+0.23
Ni..	..	..	..	+0.19
Sn..	..	..	..	+0.15
Pb..	..	..	..	+0.15
H..	..	..	..	0.00

Metals which can be Deposited in Strongly Acid Solutions.

As..	..	..	..	0.29
Cu..	..	..	..	-0.33
Bi..	..	..	..	-0.39
Sb..	..	..	..	-0.47
Hg..	..	..	..	-0.75
Ag..	..	..	..	-0.77
Pd..	..	..	..	-0.79
Pt..	..	..	..	-0.86
Au..	..	..	..	-1.08

As one sees, the division of the metals into two groups has for its basis the position occupied by hydrogen in the table of the polarisation potentials of the metals. But this position is only fixed in the practice of electrolytic analysis because platinum cathodes are always used. In fact, hydrogen has—as shown by Caspari (*Zeit. f. r. Phys. Chem.*, 1899, xxx., 1889)—a polarisation potential varying with the metal of the cathode. If one then uses, as we have done, cathodes of other metals besides platinum, the polarisation potential of hydrogen takes another position in the above table, causing a certain number of metals to pass from one group into the other.

By appropriately choosing the cathode metal, it is evidently possible to achieve the separation of two metals of the same group whose polarisation potentials are too near to be separated with a platinum cathode; a metal is chosen giving to hydrogen a polarisation potential intermediate between those of the two elements to be separated. In a strongly acid solution the element with the lowest polarisation potential will be precipitated, the bath being made a good conductor by the non-evolution of hydrogen at the cathode.

In order to choose the most suitable metal, the following table, due to Caspari, must be consulted; this gives the values of the polarisation potential of hydrogen when disengaged on different metals taken as cathode in normal sulphuric acid. (See Table II.).

But it is not enough to choose as cathode a metal which has the property of raising the polarisation potential of hydrogen above the polarisation potential of the metal to be precipitated, for this property of the cathode metal disappears when it is covered by the precipitated element, and

TABLE II.

Pt, platinised	..	..	..	0.00
Au	..	..	..	0.02
Fe (in NaOH)	..	..	..	0.08
Pt, polished	..	..	..	0.09
Ag	..	..	..	0.15
Ni	..	..	..	0.21
Cu	..	..	..	0.23
Pd	..	..	..	0.46
Cd	..	..	..	0.48
Sn	..	..	..	0.53
Pb	..	..	..	0.64
Zn (in acid zinc solution)	..	..	..	0.70
Hg	..	..	..	0.78
Cu, amalgamated	..	..	..	0.51
Pb, amalgamated	..	..	..	0.54
Cd	..	..	..	0.68

then acts as if made entirely of this precipitated element. In order that the deposition may continue, it is necessary that the precipitated metal itself should also possess the property of raising the polarisation potential of hydrogen above its proper value.

By taking cathodes made of the same metal as that to be deposited, it is seen that, according to the preceding table, it is possible to precipitate in strongly acid solutions, not only the metals whose potentials are lower than that of hydrogen (Table I.), but lead, tin, and cadmium. In fact, the polarisation potential of lead (+0.15) is notably lower than that of hydrogen when disengaged on a lead cathode, and the same can be said of tin and cadmium.

As an application of this new method of analytical separation, we will give the separation of zinc and cadmium—metals which we have not been able to separate before with a platinum cathode,* on account of the small difference of their polarisation potentials. On the other hand, we have been able to carry out the separation with a tin or cadmium cathode in a strongly acid solution. Our cathodes were none other than our platinum-gauze electrodes covered electrolytically with tin or cadmium.

The cadmium or the zinc, in the state of sulphates, were treated with 10 grms. of ammonium sulphate and an excess of 5 c.c. of concentrated sulphuric acid. The solution was diluted to 300 c.c., and a current of 0.3 ampère allowed to pass.

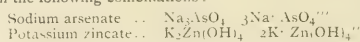
Experimental Results.

Quantities weighed.†

Cd.	Zn.	Cadmium deposited.	
0.1991	2	0.1972	Cathode of tinned platinum-gauze.
0.2990	2	0.3010	
0.1996	1	0.2002	
0.1991	2	0.1984	Cathode of platinum-gauze plated with cadmium.
0.2488	2	0.2484	
0.1991	0	0.1968	
0.2000	2	0.0002	Cathode of platinum-gauze.

III. Formation of Complex Salts.

One way of preventing a certain number of metals from precipitating themselves on the cathode, is to make them pass into the state of complex salts; that is, salts which dissociate to give, not the metallic ions, but complex ions containing the metal. For example, if we wish to make arsenic or zinc pass into the state of complex salts, we can form the following combinations:—



The complex salts have been studied from the point of

* Besides using weak acetic acid or cyanide solutions and the feeblest possible currents.

† The cadmium used in the first three experiments contained:—Pb 0.23, Fe 0.000, Zn 0.000 per cent. That used in the three following contained:—Pb 0.243, Fe 0.193, Zn 0.000 per cent. The figures given in the table as "Quantities weighed" differ from the amounts actually weighed by the quantity of impurity present.

view of their application in electrolytic analysis, especially by Frendenberg (*Zeit. Phys. Chem.*, xiii., 97).

As a matter of fact, a certain number of complex anions are partially dissociated into metal ions; the metal can then be deposited on the cathode, but will require an E.M.F. higher than the polarisation potential of the simple salts.

If in a solution of several metals some of them pass into the state of complex salts, then those metals taking the part of non-dissociable complex anions will not separate under the influence of the current, and the metals taking the part of dissociable complex ions will only separate at a higher potential than the polarisation potential of their simple salts.

This is then a means of widening the intervals between the polarisation potentials and of applying the principle of the successive separation of metals by gradual increase of the E.M.F.

The separation of antimony and tin in a concentrated solution of sodium hydrogen sulphide, as indicated by Classen, is an example of the use of complex salts. The tin here passes into the state of a complex anion.

If copper is present with the tin, the copper being slightly soluble in the sodium-hydrogen sulphide, deposits itself with the antimony. This has been shown by us (*Comptes Rendus*, 1896, cxxxiii., 1064; *Ann. de Chim. Analyt.*, 1897, 742).

We avoid this precipitation by adding potassium cyanide to the bath: this causes the copper to pass into the state of a slightly dissociated anion, which is not electrolysed by the potential employed. (For further details see Holland, "Separation and Determination of Antimony by an Electrolytic Method," *Bull. Soc. Chim.*, 1903, xxix., 262).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 26th, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A New Dilatometer, exhibited by Mr. B. BONNIKEN, was described by Mr. B. F. E. KEELING.

The instrument was originally designed for measuring the expansion of balance-wheels of watches, and has latterly been applied to the determination of the coefficient of dilatation of specimens of materials, used in the form of wires about 1½ inches in length. The increase in length with change in temperature is magnified about 1500 times by means of a chain of accurately mounted gear-wheels, the last one of which moves a pointer over a circularly graduated scale. With an ordinary specimen of steel one degree rise in temperature causes a movement of the pointer over about one-third of a scale-division, and a mean coefficient of expansion of such a substance over a range of 100° C. can be obtained to about 1 per cent in a single experiment of five minutes' duration. The instrument has been standardised by using specimens cut from bars which have been examined by Mr. Keeling in the water-bath comparator at the National Physical Laboratory.

The CHAIRMAN expressed his interest in the dilatometer, and said he had had an opportunity of seeing it in use at the National Physical Laboratory. Results were obtained easily and rapidly, and one advantage of the instrument was that it worked satisfactorily with small specimens.

Dr. W. WATSON read a paper on "A Quartz-thread Vertical Force Magnetograph."

The late Dr. Eschenhagen was the first to show that when the moment of inertia of the suspended system in a horizontal-force magnetograph is made very much smaller

than that employed in the ordinary form, it is possible to detect variations in the earth's field of quick period. The design of a satisfactory form of instrument to record rapid variations of the vertical component presents very considerable difficulties. Thus if an attempt is made to reduce to any great extent the moment of inertia, and hence the mass of the balanced magnet in the ordinary form of Lloyd's balance, it is found that irregularities are immediately introduced owing to imperfections or dirt interfering with the free movements of the knife-edge. Further, slight tremors cause the knife-edge to slip about on the plane, and thus the azimuth of the magnet varies. The instrument which the author has designed and constructed resembles, in principle, the quartz-thread gravity balance of Prof. Threlfall. In addition to the advantages derived from the suppression of the knife-edge, the instrument can be simply and accurately compensated for the effects of changes of temperature. The principle of the instrument is to have a magnet suspended on a horizontal quartz fibre kept stretched by means of a spring. The centre of gravity of the magnet and the torsion of the fibre are so adjusted that the axis of the magnet is horizontal. Any variation of the vertical force produces a rotation of the magnet about the fibre which can be suitably recorded by means of a mirror attached to the magnet. The temperature compensation is effected by weighing the magnet on the same side of the axis of the fibre as the south pole. So that the magnetic couple and the couple due to the torsion of the fibre act in the same direction. Hence, since an increase in temperature causes one of these couples to decrease and the other to increase, by suitably adjusting the weight, and therefore the magnitude of the torsion couple, complete compensation can be obtained. The suspended system in the instrument shown at the meeting consists of two magnets 8 cm. long and 1 m.m. diameter attached by means of small platinum straps to two fused rods of silica which form part of the plate of fused silica forming the mirror. The upper surface of the mirror is planitised. The fixed mirror is supported on the base of the instrument, and is capable of adjustment. The instrument has been tested at the National Physical Laboratory, and it is proposed to set up one of the instruments in the new Magnetic Observatory.

Mr. C. V. BOYS congratulated the author, and said he had had the opportunity and privilege of watching the growth of the instrument. It showed that the properties of quartz-fibres were even more perfect than anything he himself had ever claimed for them. The fact that it was possible to design and construct such an instrument in a physical laboratory showed an advance in scientific education. The theory of the instrument had been carefully worked out, and everything that had to be done practically had been done in the best possible way.

Prof. J. D. EVERETT expressed his interest in the paper, and said there was no novelty in using a horizontal fibre for a control. Horizontal wires were so used in Kelvin's portable electrometer and in the gauge of an ordinary quadrant electrometer. He thought the instrument would be improved by increasing the number of needles.

Dr. J. A. HARKER asked the author for the ordinary working sensitiveness of the instrument. When working with magnetographs of the Eschenhagen type, he had found they became unstable when the sensitiveness was increased to about three times the Kew standard sensitiveness.

Mr. T. H. BLAKESLEY asked for the period of vibration of the suspended system.

Mr. J. R. ASHWORTH sent a letter which was read by the CHAIRMAN, stating that the temperature compensation might be effected by using drawn steel wire magnets with an incremental temperature coefficient. Magnets can now be made to have, within limits, any assigned temperature coefficient (from negative, through zero, to positive).

The CHAIRMAN congratulated the author upon his success, and said that he was glad that Dr. Watson had

been able to obtain assistance from the National Physical Laboratory.

Dr. WATSON said he did not think that the magnets suggested by Mr. Ashworth would be of much advantage for vertical-force magnetographs, as there would have to be a gravity-bob in all cases in order to adjust the centre of gravity of the moving system. They might, however, be of use in a horizontal-force instrument. Replying to Dr. Harker, he said that 1 c.m. on the records corresponded to 87, whereas 1 c.m. on the Kew records represented 507. Replying to Mr. Blakesley, he said the period of vibration was large, but it was not necessarily important to have as long a period as possible. With regard to Prof. Everett's remarks, he pointed out that all metallic wires were ruled out of the question on account of elastic fatigue. He had used two magnets only because of the experimental difficulties in attaching them to their support.

A paper by Mr. G. W. WALKER, "*On Stresses in a Magnetostatic Field*," was read by the SECRETARY.

Quince found that when a glass bulb containing a solution of ferric chloride was placed between the poles of a strong electromagnet, the level of the liquid, in a capillary tube attached to the bulb, fell. This has been held to require for its explanation a system of stress which differs from the magnetic stresses of electrical type. The object of this paper is to show that the experiment can be quite well explained by the stresses of electrical type.

Dr. W. WATSON gave Some Hints on the Preparation of Diagrams.

He pointed out that many curves accompanying papers submitted to scientific societies have to be re-drawn on white Bristol board before they are suitable for reproduction by photographic processes. It is now possible to obtain blue-lined section-paper such that the lines do not show in a photograph of a diagram drawn upon it. There are many advantages in using such paper. For instance, it practically dispenses with the use of scales and T-squares. When lettering diagrams a great saving of time and a uniformity of lettering can be effected by using indiarubber type. These can be purchased cheaply in different sizes and different founts. The larger types are sold as "Easy Sign Markers," and are supplied with rods to ensure alignment and proper spacing, and also with rods by means of which the letters may be arranged upon a circular arc. A suitable ink for use with the type can be obtained by mixing Binfield's Persian black with glycerin. Using this ink for the lettering and ordinary Indian ink for the line-work of a diagram drawn on blue-line section-paper, it is possible to slightly over expose a photograph so that the section-lines are invisible in lantern-slide prints prepared from it.

Mr. R. J. SOWTER exhibited a Portable Electroscopie of high insulation and adapted to show and measure the discharging effect of radio-active substances.

Strips of gold leaf were mounted near the ends of a strip of gutta-percha tissue, leaving sufficient gutta-percha between the metal to provide the insulation. This compound strip, when doubled in two and attached to a small metal clip, constitutes a portable electroscopie which may be supported on a glass rod, by the hand, or in any convenient manner. The effects of arbitrary amounts of radium, pitchblende, and uranium oxide were such as to discharge the leaves after electrification in five seconds, five minutes, and seven and a-half minutes respectively. The discharge-curves are practically straight lines. One of the electroscopes shown had leaves 9 inches long, and for large deflections was charged by an electrophorus. As an electrophorus Mr. Sowter has found a metal tea-tray supported on three glasses, together with a piece of brown paper warmed and brushed, satisfactory.

Prof. J. D. EVERETT mentioned that he had seen the discharging effect of radium shown by means of silk tassel electrified by stroking it with a rubber glove.

Mr. C. BOYS said that many years ago he had used a tea-tray and sheet of brown paper as an electrophorus, and had obtained from it sparks up to 2 inches in length.

THE INSTITUTE OF CHEMISTRY.

THE Twenty-sixth Annual General Meeting of the Institute of Chemistry was held at 30, Bloomsbury Square, on Tuesday, March 1st, Mr. DAVID HOWARD, President, in the Chair.

The annual accounts with the Report of the Auditors having been submitted by Mr. A. Gordon Salamon, Hon. Treasurer, and duly received, Prof. TILDEN moved the adoption of the Annual Report of the Council, at the same time commenting on the general progress of the Institute. He considered it satisfactory to note that, notwithstanding the increasingly stringent regulations as to training, the very high standard of the examinations, and in spite of the loss of members by death, the number of Fellows and Associates, viz., 1098, was 251 higher than in 1894. He also commented on the scheme for the promotion of the better training of technical chemists now under the consideration of the Council.

Mr. FRISWELL seconded the report, which was then adopted.

The ballot for the election of Censors having been taken, Dr. Thomas Stevenson, Prof. J. Millar Thomson, Prof. W. A. Tilden, and Dr. J. A. Voelcker were declared elected.

The meeting proceeded to appoint Hon. Auditors, and Messrs. A. R. Ling, C. H. Cribb, and R. E. Alison were appointed.

THE PRESIDENT then delivered his Address, in which he commented on the work of the Council during the past year, on the present position of the Institute, and on the work the Council at present have in hand.

He reported that the number of candidates for the examinations continued to increase, and that it had been found necessary to make arrangements for holding an extra examination in April of this year in order to avoid an excess of candidates in July. The Council, with the help of the new Treasurer, had given particular attention to the finances of the Institute; the heavy expenditure on examinations had rendered it necessary to raise the fees, but the Council had given time for students, already in course of training, to become registered under the lower fees. The alterations would not be such as to impose a great hardship on the individual candidate, and yet, by the time the new regulations were in full operation, the fees received would probably meet the cost of the examinations. Hitherto they had been conducted at a heavy loss. It had always been felt that the maintenance of the efficiency of the examinations was a primary duty of the Institute, and, in endeavouring to organise the profession—by bringing together the properly trained and competent—it had been necessary for the Institute to afford all possible facilities for this object. The principal duty of the Institute was to promote the better education and examination of public and technical analysts. Mr. Howard showed how the Institute had carried out this object in promoting the better education of professional chemists generally, and public analysts in particular. He mentioned incidentally that, from carefully collected information, he had ascertained that in England and Wales 93.5 per cent, in Scotland 89.5 per cent, and in Ireland 84.7 per cent of the appointments as public analysts, under the Sale of Food and Drugs Acts, were held by Fellows and Associates of the Institute. However no special provision had been made in respect of the training and examination of technical chemists, and it was to this matter that the Council at the present time were paying particular attention. An outline of the proposed scheme had been published in the *Proceedings*, and details will be published shortly. The Special Committee which had the matter in hand would hold a conference during the present year with manufacturers and others interested in the progress of our scientific industries. The difficulty was to bridge over the gap between the scientific training and the practical work of the technical chemist; he has to learn to think in tons instead of grammes. The

whole question would require most careful consideration, but it was hoped that the Institute might assist in overcoming the difficulty.

The Officers and Members of Council for the ensuing year were duly elected as follows:—

President—David Howard.

Vice-presidents—George Beilby; Frederick Daniel Chataway, M.A., D.Sc.; Percy Faraday Frankland, Ph.D., F.R.S.; Edmund Albert Letts, D.Sc.; Edmund James Mills, D.Sc., F.R.S.; John Millar Thomson, LL.D., F.R.S.

Hon. Treasurer—Alfred Gordon Salamon, A.R.S.M.

Members of Council—Alfred Henry Allen; Leonard Archbutt; Edward John Bevan; Bertram Blount; Horace T. Brown, LL.D., F.R.S.; James Cameron; Alfred Chaston Chapman; Edwy Godwin Clayton; James Kear Colwell; Edward Divers, M.D., F.R.S.; James Johnstone Dobbie, M.A., D.Sc.; Bernard Dyer, D.Sc.; Thomas Fairley; Richard John Friswell; Arthur George Green; Alfred John Greenaway; Oscar Guttman; Henry James Helm, I.S.O.; Herbert Jackson; William Walker James Nicol, M.A., D.Sc.; Frederic James Montague Page, B.Sc., A.R.S.M.; William Jackson Pope, F.R.S.; Alexander Scott, D.Sc., F.R.S.; David Alexander Sutherland; Leo Taylor; Edward William Voelcker, A.R.S.M.; Sydney Young, D.Sc. F.R.S.

NOTICES OF BOOKS

Transactions of the American Electro-chemical Society. Vol. III. Third General Meeting. Published by the American Electro-chemical Society, Philadelphia, Pa. 1903. Pp. 373.

The third general meeting of this Society was held in New York on April 16th, 17th, and 18th, 1903, under the presidency of Dr. Joseph W. Richards, when a number of interesting papers were read and discussed. Some of the most important were on the "Corrosion of Metals by Electrolysis," by A. S. Knudson, with special regard to the destructive effects of railway currents upon subterranean metals, such as water-pipes; "Ions and Electrons," by Louis A. Parsons, which will be of service in extending the new theories and hypotheses which have followed on the discovery of radium; and "Determination of Vapour Densities in an Electric Furnace," by Prof. W. Nernst.

The appendix consists of a lecture delivered to the Society on April 17th by William J. Hammer on "Radium and other Radio-active Substances, with a consideration of Phosphorescent and Fluorescent Substances; the Properties and Applications of Selenium and the Treatment of Disease by the Ultra-violet Light." In the rather wide limits of this comprehensive title, the author has endeavoured to describe certain fundamental principles connected with the phenomena upon which he has treated; and in considering these subjects, all of which may be said to be on the borderland of science, to bring out by means of experiments, lantern-slides, and illustrations, the practical and commercial side.

The Optical Rotating Power of Organic Substances, and its Practical Applications. By Dr. HANS LANDOLT. Second Edition. Authorised English Translation, with Additions by Dr. J. H. LONG. Illustrated. Easton, Pa.: The Chemical Publishing Company. 1902. Pp. 751.

The scope of the second edition of this work, published in 1898, and of which the present volume is a translation, is much wider than that of the first. The progress which has been made of late years in the field of optical activity rests, so far as the theoretical side is concerned, mainly upon the great interest aroused among chemists by the hypothesis of

van't Hoff and Le Bel on the relation between rotating power and the atomic structure of carbon compounds.

In a practical direction progress has been made in the improvement of apparatus and in the methods of optical analysis; while the number of optically active substances known has increased since 1879 from 300 to over 700.

The book is divided into six parts. Part I. is on the general conditions of optical activity, and includes the classification of active substances, the nature of the rotating power, the relations between rotating power and chemical constitution of carbon compounds. Part II., on the physical laws of circular polarisation, is only a short one, while Part III., on numerical values for the rotating power and specification rotation, covers many more pages.

The fourth part deals with apparatus and methods for the determination of the specific rotation, and Part V. is on the practical applications of optical rotation, such as the determination of cane-sugar, of milk-sugar, of glucose, of maltose, camphor, the cinchona alkaloids, &c.

Part VI. is on the constants of rotation of active bodies, to which many additions have been made by the translator, by permission, and with the assistance, of the author.

The book is one of considerable value and importance, and will be studied to much advantage by those who have identified themselves with this particular branch of science.

Fractional Distillation. By SYDNEY YOUNG, D.Sc., F.R.S. With 72 Illustrations. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1903. Pp. 284.

Fractional distillation is invaluable when we wish to prepare liquids in the highest state of purity, and the eighteen years' experience of the author in researches requiring the frequent use of this manipulative method, entitles him to speak with authority on the subject. One important result of his careful investigation of the subject has been the devising of new methods and apparatus which have been described from time to time in the scientific journals.

The book is divided into nineteen chapters, and is fully illustrated. After a few preliminary chapters on more or less theoretical and elementary points, we come to Chapter VII., on "Directions for Carrying out a Fractional Distillation"; this is followed by chapters on the theoretical relations between the weight and composition of the distillate, and between the boiling-points of the residue and the distillate.

Chapters X., XI., and XII. deal with modifications of the still-head, dephlegmators, and "regulated" or "constant temperature" still-heads, and Chapter XV. is on distillation on a manufacturing scale. The application of fractional distillation to quantitative analysis is dealt with in Chapters XVI., XVII., and XVIII.; this method may be safely employed in the majority of cases for the determination of the composition of a mixture which separates normally into its components, provided that a very efficient still-head be employed and the operation be carried out very slowly. Chapter XIX. contains general remarks on the purposes for which fractional distillation is required; the interpretation of experimental results, the choice of still-head, and number of fractions, &c. The book, which is a valuable one, concludes with a short appendix on the correction of the height of the barometer for temperature, and a good comprehensive index.

Aids to Forensic Medicine and Toxicology. By WILLIAM MURRELL, M.D., F.R.C.P., &c. Sixth Edition, Fourteenth Thousand. London: Baillière, Tindall, and Cox. 1903. Pp. 110.

This book is not intended as a substitute for ordinary textbooks on forensic medicine or for lectures, but simply as an aid or reminder of facts already acquired.

Forensic medicine, or medical jurisprudence, is that portion of medical science which treats of the connection

between law and medicine, and deals with cases connected with the administration of justice, while toxicology treats of the nature and detection of poisons. These are both important branches of medical science, and the present "aid" deals with both in a clear and concise manner, and will be of service to medical men in general.

General Information with regard to the Gold, Diamond, and Forest Industries of British Guiana. Edited by the Secretary of the Institute of Mines and Forests of British Guiana. Georgetown: Printed for the Government of British Guiana by Baldwin and Co. 1903. Pp. v.-25, xxiv., and xviii.

As frequent inquiries are addressed to the Colonial Office with regard to mining, &c., in British Guiana, it has been thought desirable, in the interests of the colony, to prepare and bring up to date annually a special pamphlet giving shortly the necessary information as to the gold and diamond mining industries, and the land and mining regulations, to supplement the information contained in the handbook issued by the Emigrants' Information Office. In these pages will be found information and statistics with regard to the Ballata and timber industries, as well as those of gold and diamond mining. Notes on the method of acquiring Crown lands, a digest of the mining laws of the colony, hints as to equipment, and geological notes are included, together with information as to communication with the colony, and in the colony with the gold and diamond fields.

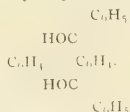
This handbook will be of service to those intending to proceed to British Guiana; the information it contains is of a varied but sound character, but it has been put together in a most inconvenient manner; though only a small volume no fewer than four systems of numbering the pages have been adopted, besides several scattered indices and appendices, the pages of which are not numbered at all. As it is proposed to issue this handbook annually, we hope to see the next edition pagged in a more rational manner.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are in centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxviii., No. 6, February 8, 1904.

Action of Phenylmagnesium Bromide on Anthraquinone. Symmetric γ -Dihydroxyl- γ -diphenyl Dihydride of Anthracene.—A. Haller and A. Guyot.—The authors apply M. Grignard's method to the preparation of γ -dihydroxyl- γ -diphenyl dihydride of anthracene:—



Flame Spectra of the Alkaline Metals.—C. de Wauville.—The author examines the spectra of lithium, sodium, and potassium, and his experiments tend to verify the theory that the production of spectrum lines is purely calorific. This theory explains the fact that in the arc, where the temperature is considerably higher than that of the flame, there are more elementary zones; that is to say, more special states in which the atom is susceptible of emitting a given series of rays.

Use of Alternating Currents for Electrolysis.—André Brochet and Joseph Petit.—The authors make a series of interesting experiments on the solubility of copper in potassium cyanide under the influence of alternating currents.

Formation of Phosphorus Sulphides in the Cold.—R. Boulough.—Certain phosphorus sulphides can be produced in the cold if a little iodine is added to a solution of sulphur and of P_2S_3 . The violet colour rapidly disappears, and in a day or two small crystals appear, which on analysis are shown to have the invariable composition P_4S_5 .

Action of Heat and Light on Mixtures of Phosphorus Sesquisulphide and Sulphur in Carbon Disulphide Solution.—E. Dervin.—The author finds that heat and light act in the same manner on mixtures of sulphur and phosphorus sesquisulphide in carbon disulphide solution. A solution containing one molecule of P_4S_3 to a half molecule of sulphur gives yellowish transparent needles of P_2S_4 . He also ascertains that solar light completes the reaction in a month or two, whilst at a temperature of 210° the same effect is produced in two hours.

Action of Carbon Dioxide on Solutions of Sodium Nitrite.—C. Marie and R. Maquis.—The authors repeat certain very simple experiments which show decisively that carbon dioxide displaces nitrous acid in solutions of sodium nitrite.

Constitution and Properties of Vanadium Steels.—Léon Guillet.—The author distinguishes three distinct groups in crude vanadium steels, one of these groups being intermediate in properties between the other two. He also describes the mechanical properties of each of the groups, and shows that the steels of each present very remarkable characteristics. Lastly, he determines the fact that only vanadium steels containing less than 7 per cent of vanadium are susceptible of industrial application, on account of the fragility of those containing larger percentages of vanadium.

Allotropic Transformations of Nickel Steels.—O. Boudouard.—The author investigates the allotropic transformations of certain specimens of nickel steels containing 2 per cent and 30 per cent of nickel by means of curves obtained during the heating and cooling of bars of the metal.

Diurides. Homoallantoic Ether.—L. J. Simon.—In a previous research the author proved the existence of homoallantoic ether, $\text{CH}_3\text{—C}(\text{NH—CO—NH}_2)_2\text{—CO}_2\text{C}_2\text{H}_5$. This diuraminic ether, the only one known up to the present time, is obtained by the direct action of urea on ethyl pyruvate without the intervention of any condensing agent. When pure it is a white powder, micro-crystalline, and decomposed at 200° ; insoluble in water and most organic reagents. He also investigates certain of the chemical properties of this substance.

Phosphoric Ethers of Glycol.—P. Carré.—Glycol, in the same manner as glycerin, can react on the three oxyhydrides of phosphoric acid, giving rise to three ethers. The best results are obtained by acting at a temperature of $140\text{—}145^\circ$, and under a pressure of 15 to 18 m.m., given by a water-pump. Under these conditions the maximum etherification is attained after ten hours of heating. The mixture then contains 3.5 per cent of the triether, 42.4 per cent of the diether, and 44 per cent of the monoether, giving a total of 89.9 per cent of combined acid.

Biochemical Synthesis of Olein and certain Ethers. Henri Pottevin.—In a previous investigation the author proved that oleic acid and glycerin are etherified under the influence of a pancreatic ferment, giving monolein. In consequence of the same diastatic action, he is now enabled to prepare triolein identical with natural olein.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Miss L. A. Black, H. T. Davidge, H. F. Dickens, K.C., F. S. Eve, F. L. M. Forster, Miss C. E. M. Gibbons, T. G. Hull, Vivian B. Lewes, Mrs. Gerard Leigh, The Hon. Mary Portman, H. R. Prendergast, W. N. Shaw, F.R.S., J. Sorley, Dr. R. H. Scanes Spicer, The Hon. Sir Joseph Walton, and E. Wormald were elected Members.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, March 15, at 5 o'clock, Dr. E. A. Wallis Budge will deliver the first of two lectures on "The Doctrine of Heaven and Hell in Ancient Egypt, and the Books of the Underworld"; and on Thursday, March 17, at the same hour, Mr. Sidney Lee commences a course of two lectures on "Shakespeare as Contemporaries knew him." The Friday Evening Discourse on March 18 will be delivered by M. Henry Arthur Jones on "The Foundations of a National Drama"; and on March 25 by Professor Dewar on "Liquid Hydrogen Calorimetry."

Relative Effects of Superphosphate and Basic Slag upon the Feeding Quality of Swedes.—The West of Scotland Agricultural College has published, in pamphlet form, the results of a number of tests made on the above subject by Dr. John W. Paterson. The present experiment was designed to test the effects of manures upon quality by utilising the swedes grown for an accurate feeding test. One acre of roots was manured with superphosphate and one acre with basic slag, the same quantities of nitrogen and potash being added to each plot. The roots on each acre were subsequently fed to separate lots of sheep. The yield of roots from the first plot was 21 tons 0 cwt. 3 qrs., and from the second plot 19 tons 18 cwt. 0 qrs., the superphosphate producing the heavier crop. The two crops were then fed to two lots of selected sheep, 40 in each lot, the same weight of roots being given to each lot. Besides roots, a weighed and equal amount of dried grains was given daily to each lot. Hay was not considered necessary when dried grains was the concentrated food. The sheep were weighed on two dates after the commencement to find their respective gains, and it was found that while, during the first half, the two lots of sheep increased by nearly the same amount, during the second period the basic slag lot took a somewhat strong lead. Over the whole period the basic slag lot of 40 sheep made nearly 15 per cent more increase, although the sheep were otherwise similarly treated in every way. Taking the weight of crops alone, the basic slag stood to superphosphate as 94 to 100; but when actual mutton production is reckoned in, the tables are turned, and basic slag stands to superphosphate as 108 to 100. That is to say, the slag acre produced the smaller but the more valuable crop.

The Compounds of Sulphur and Tellurium.—A. Gutbier and F. Flury.—I. *Action of Sulphuretted Hydrogen on the Compounds of Hexavalent Tellurium.*—The authors confirm the previous results of Brauner (*Chem. Soc.*, 1895, vol. lxxv., p. 545). In aqueous solution of telluric acid, SH_2 , at the ordinary temperature, gives a precipitate of the composition TeS_3 , but which may be looked upon as a mixture of sulphur and tellurium. In a warm solution, sulphuretted hydrogen partially reduces the TeO_3 to the state of tellurous acid. In this reaction no sulphoxytelluric acid is formed. II. *Action of Sulphuretted Hydrogen on the Alkaline Solutions of Hexavalent Tellurium.*—The authors have not succeeded in isolating any sulphotellurates, which confirms the doubts expressed by Staudenmeyer (*Zeit. Anorg. Chem.*, 1895, vol. x., p. 189) on the results announced by Oppenheim (*Journ. für Prakt. Ch.*, [1], vol. lxxi., p. 270). III. *Action of Sulphuretted Hydrogen on Solutions of Tetraivalent Tellurium.*—In acid solution sulphuretted hydrogen causes the precipitation of an orange-red material of the composition TeS_2 . This precipitate is a mixture of S and of Te. By extracting in a Soxhlet apparatus with sulphide of carbon, the major portion of the sulphur is eliminated (the residue contains only 1.18 per cent of S). From the residue containing 1.18 per cent of sulphur, the authors have succeeded in obtaining tellurium free from sulphur, and they are continuing their researches with a view to clearing up this particular point. The paper closes with a note by M. Gutbier concerning

the criticism his previous work has received at the hands of M. Brauner (*Zeit. Anorg. Chem.*, vol. xxxi., p. 378).—*Zeit. Anorg. Chem.*, vol. xxxii., p. 272.

Action of Phenylhydrazine on the Oxidised Compounds of Selenium and Tellurium.—A. Gutbier.—In hydrochloric solution tellurous acid is reduced by phenylhydrazine at the ordinary temperature. In aqueous solution the same reduction takes place, with the transitory formation of an unstable bright yellow precipitate. Selenious acid dissolved in dilute alkali and treated with phenylhydrazine behaves like TeO_2 . In cold alkaline solution we can obtain a pseudo-solution of selenium in alcohol, but this very unstable solution deposits selenium rapidly. The reduction of SeO_3 is slower, and the author has succeeded in isolating the intermediate product, $(\text{C}_6\text{H}_5\text{NH})_2\text{NH}_2\text{SeO}_2\text{H}_2$, in the form of small microscopic needles having a silky lustre, stable in the air, and soluble in water. This colourless solution deposits Se when raised to boiling-point in the presence of a few drops of hydrochloric acid.—*Zeit. Anorg. Chem.*, vol. xxxii., p. 257.

A New Reaction for Aldehydes. E. Rimini.—It has been shown in a previous paper that the aldehydes condense with nitrohydroxylic acid, giving the hydroxylic acids. This reaction allows of the isolation of the latter acid with difficulty, on account of the formation of a nitrite which, by the acidulation of the solution, changes the product through the oxidising action of the oxides of nitrogen. The author uses benzene-sulphohydroxylic acid, $\text{C}_6\text{H}_5\text{SO}_2\text{NHOH}$, which acts like the nitro acid but gives benzene-sulphonic acid, which does not interfere with the isolation of the hydroxylic acid sought for. This latter is precipitated in the form of a cupric salt by the addition of acetate of copper to the aqueous acetic solution. The author has operated with formic, acetic, valeric, amino-valeric, acrylic, citral, glyoxal, glyceric, benzoic, piperonylic, anisic, salicylic, and furalic aldehydes. Formic acid, however, gives the same reaction, as it contains the aldehydic group; the author also gives the analysis of the salts of copper obtained with these different substances. He proposes to examine the application of this reaction to the qualitative and quantitative detection of the aldehydes present in alcohol and in spirits.—*Gazz. Chim. Ital.*, vol. xxxi., (2), p. 84.

Mixed Crystals of Sulphur and Selenium.—W. E. Ringer.—Sulphur and selenium in the fused state are miscible in all proportions; the melted mass containing a proportion of selenium greater than 10 atoms per cent crystallises with difficulty. On cooling very slowly an amorphous mass is produced. By heating them for several hours to very near their fusing-point, mixtures rich in selenium become completely crystalline. From an examination of their fusion curves, it results that all these crystalline mixtures consist of mixed crystals of sulphur and selenium; nothing points towards the formation of a double combination. These melted mixtures form three series of crystals.—1. A series of monoclinic crystals containing from 0 to 27 atoms per cent of selenium and of the same type of crystal as monoclinic sulphur. 2. A series of monoclinic crystals containing 50 to 82 atoms per cent of selenium (of the same type as the third modification of sulphur?). 3. A series of crystals formed of hexagonal rhombohedra of the type of metallic selenium, containing 87 to 100 atoms per cent. At a temperature comprised between 75 and 95.5 the crystals of the first series are transformed into orthorhombic crystals; the transformation is comparable to that of monoclinic sulphur into the orthorhombic variety. The crystals belonging to the two other series do not undergo any analogous change. At the ordinary temperature we obtain:—1. A series of rhombic crystals containing from 0 to 10 atoms per cent of selenium. 2. A series of crystals containing from 55 to 76 atoms per cent of selenium. 3. A series of crystals of the type of hexagonal selenium containing 90 to 100 atoms per cent of selenium.—*Zeit. Anorg. Chem.*, vol. xxxii., p. 183.

Detection of Saccharine by New Reactions.—M. Spica.—The author criticises the method of detecting saccharine by heating the product of the extraction with ether mixed with ligroin, with resorcin, and sulphuric acid. This method, though very sensitive, has the drawback of giving fluorescences with the ethereal extracts of wines and the various pharmaceutical syrups free from saccharine. This is a result of the entangling by the ether of the tannic, lactic, tartaric, malic, succinic, and other acids, capable of forming fluorescent products of condensation with resorcin. The author prefers the two following methods:—1. *Oxidation of the Saccharine and Detection of the Nitric Acid with Diphenylamine.*—He operates in a test-tube with the residue from the evaporation of the ligroin-ether which served for the extraction. H_2SO_4 and a crystal of KMnO_4 are added, and the tube heated gently; the MnO_2 is destroyed with a few drops of oxalic solution, and after the addition of a few c.c. of hydrochlorate of diphenylamine, concentrated sulphuric acid is poured slowly in, and the surface of contact of the two liquids observed closely; a blue ring should be produced. 2. *Transformation of the Saccharine into Aminobenzoic Acid, and the Formation of an Azoic Colour.*—The residue from the extraction, containing saccharine, is treated with a few decigrams of caustic lime. Heat until slight browning occurs, treat with water, decant the aqueous solution, acidulate with HCl , and add a granule of zinc; let the reduction proceed for twenty minutes, then decant the clear liquid, and treat with a few drops of a dilute solution of NO_2Na , and finally 5 drops of α -naphthylamine solution. A cherry-red colour is then observed if saccharine is present.—*Gazz. Chim. Ital.*, vol. xxxii, [2], p. 41.

Composition of Potato Starch.—A. Fernbach.—The author establishes the fact that potato starch is not a homogeneous substance owing to its being deposited in concentric layers, which differ in composition. He finds the chief irregularity in the composition lies in the proportion of phosphorus present in the starch.—*Comptes Rendus*, cxxxviii, No. 7.

MEETINGS FOR THE WEEK.

MONDAY, 14th—Society of Arts, 8. (Cantor Lectures). "Recent Advances in Electro-chemistry," by Bertram Blount, F.I.C.

TUESDAY, 15th—Royal Institution, 5. "The Doctrine of Heaven and Hell in Ancient Egypt, and the Books of the Underworld," by E. A. Wallis Budge, M.A., &c. Society of Arts, 4.30. "Recent Developments in Devonshire Lace Making," by Alan S. Cole, C.B.

WEDNESDAY, 16th—Society of Arts, 8. "Artificial and other Building Stones," by L. P. Ford.

Microscopical, 8. "A Note on some New Methods of Measuring the Magnifying Power of the Microscope and of Lenses generally," by Prof. A. E. Wright. Exhibition of Hand-painted Lantern Slides, illustrating Botanical Histology, prepared by A. Flatters.

Chemical, 5.30. "Mercuric Nitrite and its Decomposition by Heat," by P. C. Ray. "Note on the Higher Glycerides," by J. B. Hannay. "Nature of a Solution of Iodine in Aqueous Potassium Iodide," by C. H. Burgess and D. L. Chapman. "Reduction of 2:6-Dinitrotoluene with Hydrogen Sulphide," by J. B. Cohen and J. Marshall. "Isomeric Change of Diacylhydrides into Acyl-amino-ketones—Transformation of the Dibenzoyl Toluidines into the Isomeric Methyl-benzoyl-amino-benzophenones," by F. D. Chattaway and W. H. Lewis. "Acid Esters of Methyl-substituted Succinic Acids," by W. A. Bone, J. L. Sudborough, and C. H. G. Sprankling. "Action of Ethyl β -iodopropionate on Ethyl Diiodoacetylacetate-tetracarboxylate," by O. Silberrad.

THURSDAY, 17th—Royal Institution, 5. "Shakespeare as Contemporaries knew him," by Sidney Lee, Litt.D.

FRIDAY, 18th—Royal Institution, 9. "The Foundations of a National Drama," by Henry Arthur Jones.

SATURDAY, 19th—Royal Institution, 3. "The Life and Work of Stokes," by Right Hon. Lord Rayleigh, F.R.S.

THE RHIWLAS ALUMINOUS & SILICIOUS EARTH, F.O.R., FRONGOCH STATION, G.W.R. SECOND PRIZE, CHICAGO EXHIBITION.

So long and favourably known in the Brown and Coloured Paper, Paint, Grease, Boiler Composition, Rustian, Soap, Disinfectant, Cleansing, and other trades, can be obtained, or samples and particulars of either Buff or Grey Mineral, from THE AGENT, Rhiwlas Estate Office, Bala, Merionethshire.

The late Manager having accepted another situation, propositions will be considered for a Syndicate or Partnership; also proposals to purchase two well situated Slate Quarries (Festiniog quality) and a valuable Cement proposition.

CHEMICAL LABORATORY, WIESBADEN, GERMANY.

DIRECTORS.

Practical Instruction in the Laboratory Prof. H. FRESENIUS, Ph.D.
Prof. W. FRESENIUS, Ph.D.
Prof. E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) Prof. H. FRESENIUS, Ph.D.
Experimental Physics Prof. W. FRESENIUS, Ph.D.
Stoichiometry L. GRÜNHUT, Ph.D.
Organic Chemistry R. FRESENIUS, Ph.D.
Chemical Technology Prof. H. FRESENIUS, Ph.D.
Microscopy, with exercises in Microscopic work Prof. E. HINTZ, Ph.D.
Chemistry and Analysis of Foods Prof. Dr. med. G. FRANK.
Hygiene J. HUBER.
Practical exercises in Bacteriology
Technical Drawing, with exercises

The next Session commences on the 25th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL's Verlag, at Wiesbaden, or to one of the Directors.

CROOM & CO.

COPPER OVENS & BATHS.

Accurately constructed to Customers' requirements.

Estimates free by return of post.

MAKERS TO THE TRADE.

75, LEADENHALL STREET, E.C.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1s. 6d. each.

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGDON ST., E.C.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION, FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.
LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2312.

A STUDY OF THE RADIO-ACTIVITY OF CERTAIN MINERALS AND MINERAL WATERS.*

By Hon. R. J. STRUTT, Fellow of Trinity College, Cambridge.

PART I.

A CONSIDERABLE number of minerals are known in varying degrees to be radio-active. Lists have been given by M. and Mme. Curie (Thèse présentée à la Faculté des Sciences, Paris, p. 19; *CHEMICAL NEWS*, LXXXVIII., p. 85), and by Sir William Crookes (*Proc. Roy. Soc.*, LXVI., p. 411). Except in the case of pitchblende, little has been done to determine the nature of the radio-active constituents; or to decide whether any hitherto unknown radio-active body is present.

To obtain complete information on these subjects, the only method available would be to completely analyse the mineral, and examine every precipitate and filtrate for radio-activity. This process is, of course, very tedious, and the results have to be interpreted with care, since traces of radio-active elements may often be carried down in the groups to which they do not properly belong, and thus cause confusion. A much easier method is to heat the crude mineral, and to examine the rate of decay of the emanation which it gives off. Each emanation has a characteristic time constant of decay, and by determining this we can identify it.

The method is, of course, useless for testing the presence or absence of radio-active elements, such as uranium,† which do not give off a characteristic emanation. But the great facility with which it may be applied to a small quantity of material, and the definiteness of the results, are great merits.

In any case when a material suspected to contain radium is obtainable in abundance, it is better to test for the presence of emanation than to look for activity in the solid. For but little of the solid material can be advantageously used in the test. Thick layers give no larger effect than thin ones, since the upper layers absorb the radiation from the lower. But the emanation can be extracted from any desired bulk of material, and the effect proportionately increased. If carbonic acid or any other gas is evolved at the same time in inconvenient quantities, it can be absorbed with a suitable reagent, and the emanation contained in it thereby concentrated.

The present paper gives the results of an examination of certain radio-active materials by this method.

No new emanation has been recognised. The results have in all cases been attributable to thorium and radium.

If any emanation decidedly more permanent than that of radium existed in the evolved gas, the method could not fail to detect it. For in every case the activity of the gas was watched until it became comparable with the very small activity due to the walls of the vessel. If a more durable emanation had been present, even in small quantities, the proportion of it present would have increased relatively to the radium emanation, and its presence would have become apparent towards the end, by a diminished rate of decay.

Small quantities of an emanation less durable than that of radium might have escaped detection; for they would have been masked by the much greater quantity of the latter.

By measuring the rate of leak due to the accumulated emanation from a weighed amount, the proportion of radium present may be estimated. A comparison with the leak due to the emanation of a known weight of radium must of course be made. For this purpose it would be best to weigh out, say, a milligram of radium bromide, dissolve it in a litre of water, and evaporate a small measured quantity of the solution in a suitable tube. In this way the effect due to a standard quantity could be determined.

The method of experimenting was as follows:—

The powdered mineral was placed in a hard glass combustion tube, drawn out and sealed at one end, connected to a mercury gas-holder at the other. The mineral was heated to redness, and the gaseous products collected in the gas-holder. When the evolution of gas had ceased, the point was broken off, and air drawn into the gas-holder up to a standard volume.

For measuring the electrical effects, an electroscope was used. This was exhausted, and the gas extracted from the mineral, together with the air which had been used to make up its volume to a sufficient amount, was admitted. After a few hours, enough for the deposited activity to attain its full value, the rate of leak was read. The day and hour was noted, and the gas was pumped out into a test-tube, and stored over mercury. After a sufficient time had elapsed, it was again introduced into the apparatus by means of a syphon gas pipette,* and the rate of leak again measured. In the meantime the apparatus had been available for making measurements with other gases.

In some cases the emanation was initially so strong that it could not be conveniently investigated. In such cases a portion of the gas was diluted with air for measuring the rate of decay at first. The concentrated material was kept until, by lapse of time, it had become weak enough to be conveniently used. Its activity was followed until it had become too small for measurement.

With this preface the results for the various minerals tried may be given in the form of a table. The rates of leak are given in scale divisions per hour. When air alone filled the apparatus, the rate of leak was 2.25 sc. div. per hour. This was in each case subtracted. (Table I.).

All the minerals give radium emanation, though in very varying quantity.

These tests were not started quickly enough to give information as to the presence of a very quickly decaying emanation. This was tested for independently.

The mineral malaconite is of peculiar interest, because it has been found to contain argon as well as helium (Ramsay and Travers, *Proc. Roy. Soc.*, vol. LXIV., p. 131). Helium is formed by the degeneration of radium, and it is reasonable to assume that the other kindred gases have had a similar origin. It was hoped, therefore, that malaconite might contain some new radio-active element. It is still possible that it does so, but, if so, this substance gives no emanation distinct from that of radium.

The meteorite of Augusta, Co. Virginia, has also been found to contain argon and helium. But no emanation at all could be obtained from 20 grms. of it.

The minerals were all tested for thorium emanation by drawing air over them in the cold; the only one in the above list that gives it is the Norwegian monazite, and even this does not yield it very abundantly. A crystal of thorite, however, kindly lent me by Professor Lewis, was found to give torrents of thorium emanation. Air drawn over it in the cold possesses strong discharging power. It was not permissible to heat the specimen, which might have injured it, so that the presence or absence of radium emanation in thorite could not be investigated.

There can be no doubt that the other specimens of monazite contained thorium, for they were given me by the late Mr. W. Shapleigh, who was connected with the thorium industry, and used these varieties of monazite for preparing thorium. They were, moreover, markedly radio-

* A Paper read before the Royal Society, March 1, 1924.

† I have found a distinct, though feeble, emanation from re-crystallised uranium salts, having a rate of decay equal to that of the radium emanation. Whether this is really due to uranium, or to traces of radium, which the uranium still contains, must be left for the present as an open question.

* The methods of manipulation used in storing and transferring the gases without loss were those described in Dr. Travers' book "The Study of Radioactivity".

TABLE I.

Mineral.	Locality.	Quantity taken, in grms.	Rate of leak due to emanation (sc. div. per hour).	Rate of leak per 100 grms.	Time, in days, taken by the emanation to fall to half its initial value.
Samarskite . . .	North Carolina, U.S.A. . .	20	20,600	103,000	3'48
Fergusonite . . .	Norway?	7	4,280	61,000	3'80
Pitchblende . . .	Cornwall	40	11,900	29,800	3'50
Malacone	Hitteroe, Norway	20	1,440	7,200	3'81
	Norway	51	2,060	4,000	3'50
Monazite	North Carolina	82	37	45	3'81
	Brazil	54	11	24	3'80
Zircon	North Carolina	60	24'6	41	4'05

TABLE II.

Material.	Quantity taken, in grms.	Rate of leak due to emanation (sc. div. per hour).	Rate of leak due to emanation from 100 grms.	Time, in days, taken by the emanation to fall to half its initial value.
King's Spring, Bath . . . { Deposit from inside of well	10	250	2500	3'60
.. { Deposit from tank	12	78'2	650	—
.. { Saline residue from water	18	12'4	69	—
Old Royal Spring, Bath. . { Deposit from channel near well	10	63'5	635	—
.. { Deposit from bottom of tank	15	60	400	—
Hard deposit from sides of tank	25	43	173	3'58
Buxton deposit	26	350	1370	3'81

active, while the amount of radium emanation obtained from them was so small that their activity could not be mainly due to radium. They probably contain the thorium in what Rutherford and Soddy call the de-emanated condition. That is, the thorium emanation, though formed, is not able to escape.

It is a remarkable fact that these varieties of monazite, though they contain practically no radium, yield helium in fair quantity. There are several explanations possible. The radium originally present may have almost completely decayed into helium, and any other products which it may yield; or it may be that thorium, as well as radium, yields helium by its decomposition; or, lastly, the helium may not, in this instance, have been generated by radio-active changes at all.

It is interesting to know whether the minerals retain all the radium emanation which they generate when heat is not used to expel it. Two cases were examined. 114 grms. of powdered samarskite were kept for three weeks in a sealed glass tube. The air was pumped out and tested. It was found to contain about 1/150 part of the emanation, which could have been extracted by heat.

A similar experiment with malacone showed that about one-fiftieth of its emanation was able to escape in the cold.

It appears therefore that these minerals retain nearly all their emanation. The same is probably true of the helium produced by the emanation. Samarskite which had been heated to redness was found to retain its emanation in the cold about as well as before.

PART II.

I happened to possess a small sample of a red deposit, coloured by iron, which is left by the water of the King's Spring, at Bath. It occurred to me that it might be worth while to test this for radio-activity. The result was to show that the deposit was markedly active. On leaving it in the testing vessel (which was closed airtight) for a few days, the activity was found to increase to several times its initial value. This shows that the deposit gives off an emanation freely, even without heat.

Experiments were then made to test the rate of decay of this emanation. It proved to be identical with the rate of decay of the emanation of radium.* The activity is wholly due to that element.

In the first experiment made, I obtained a small residual leak when the radium emanation had decayed. This was attributed to a new emanation, of greater durability. But I have failed to repeat the experiment, and am forced to conclude that the leak was due to a failure of the quartz insulation, owing to the presence of moisture. It is very difficult to understand how this can have happened, for the gas was passed through drying tubes. When the rate of leak was tested with air in the apparatus, it had always a perfectly definite and constant small value.

This deposit was collected inside the King's Well itself, where the hot water issues from the ground. Other deposits are left in the tanks and pipes. They are less active than that collected near the source.

Deposits from another of the hot springs at Bath, that known as the Old Royal Spring, have also been tested. These were found to be active also. In this case there was no opportunity of collecting the deposit at the well-head itself, but it was found that the deposit left in the channel near the source was more active than that in the tanks further from it.

It was interesting to determine whether the water itself contained any radium in solution. There could be little doubt that there must be traces left in solution, after the deposit had settled out. But since the Bath water contains abundance of sulphates, and since radium sulphate is one of the most insoluble salts known, there could not be more than the merest traces present. The sulphate of barium is very much less soluble than that of strontium. And presumably the sulphate of radium is much less soluble still. Barium sulphate requires half a million times its weight of water to dissolve it; radium sulphate perhaps several hundred million times its own weight.

About 10 litres of the Bath water were evaporated to dryness. The resulting saline residue was sealed up in a hard glass tube, and left for about a fortnight to generate a stock of emanation. On heating, a distinct emanation was obtained, giving several times the rate of leak that air did. A deposit, similar to that from the Bath water, but black in colour, can be collected from the source of the hot springs of Buxton. It has been analysed by Dr. J. C. Thresh (*Proc. Chem. Soc.*, January 17, 1882), and I am indebted to his kindness for a specimen of it. This deposit was found to contain radium also; the proportion present being not very different from what was found in the case of some of the Bath deposits.

Table II. gives the quantitative data for these emanations from these deposits. The rates of leak are on the same scale as those in Table I.

It will be seen that the richest of the deposits is some thirty-six times more active than the salt obtained by evaporating the water.

Although the agreement in the rate of decay of the emanation seemed sufficient to prove that the activity was really due to radium, yet it was thought desirable to show that the chemical properties of the active constituent were in agreement with this conclusion. 200 grms. of the richest deposit were treated with dilute sulphuric acid. The activity was all in the insoluble residue, which was dirty white in colour, and amounted to about half of the entire quantity of deposit. The residue was boiled with strong sodium

carbonate solution. This was washed away, and the mass extracted with hydrochloric acid. The hydrochloric acid solution gave a slight precipitate with sulphuric acid. This precipitate was collected, and found to be strongly active, so that there is every reason to conclude that the activity of the deposit is due to the presence of radium.

The presence of radium in the Bath water and deposits is of special interest because of the occurrence of helium in the gas which rises with the spring (Rayleigh, *Proc. Roy. Soc.*, vol. lx., p. 56). There can be little doubt that the helium owes its origin to the same store of radium that supplies the water.

It is interesting to estimate the quantity of radium annually delivered by the spring. Part of this is in the deposit; part in the water. But the annual yield of deposit does not exceed a few hundred-weight at the most. And although it is much richer in radium than the dissolved salt, the quantity of the latter is so enormously greater, that the deposit may be neglected. According to the estimate of Sir A. C. Ramsay, the late Director of the Geological Survey, the salt annually delivered by the spring would be equivalent in volume to a column 9 feet in diameter and 140 feet high. Taking the density to be twice that of water, this would weigh about 500,000 kilograms.

Now the saline residue gives about 1/1500 part of the quantity of emanation that samarskite gives. Let us assume that the latter contains one-millionth part of radium, which is, I think, an outside estimate. At that rate, the annual delivery of radium by the spring amounts to about one-third grm. The volume of gas which the spring delivered is about 100 cubic feet per day (Williamson, *Brit. Assoc. Reports*, 1865, p. 380). About 1/1000 part of this is helium, so that about 3 litres of helium is given off daily, or about 1000 litres per annum. The proportion of helium to radium thus indicated is of the same order as in the radio-active minerals, though somewhat larger. This is in accordance with the view that the spring draws its supplies from the disintegration of such minerals. In obtaining the various materials from the Bath springs, I have had the great advantage of Mr. Sydenham's help. His knowledge of everything connected with the springs has been of great assistance.

In addition to the Bath and Buxton waters I have examined several others.

A sample of the Cheltenham saline water, and also a deposit left in the pipes, was kindly sent me by Mr. G. Ballinger. But no emanation could be obtained, either from the dissolved salts or from the deposit.

The boiler crust from a domestic hot-water pipe, Terling, Essex, was examined, but the result was again negative.

THE ELEMENTS: VERIFIED AND UNVERIFIED.*

By CHARLES BASKERVILLE, Ph.D., F.C.S.,
Smith Professor of General Chemistry, University of North Carolina

(Continued from p. 125.)

I HAVE referred somewhat in detail elsewhere to the factors producing variations in the absorption, as well as the advantages and disadvantages of the phosphorescent and reversal spectra ("The Rare Earth Crusade," *loc. cit.*).

Without doubt the spectroscopic criteria are the most valuable we have in judging finally the elements, and mayhap will remain so; but in my humble opinion, such have not alone sufficient authority, as yet, to usher the aspirant to a place among the elect. The contention frames itself, however, in an expression of the need for uniformity.

Whether we follow the most advanced metaphysical-chemical teachings or no, if there be any one concept upon which modern practical chemical thought depends, it is the law of definiteness of composition. There may be, and doubtless are, definite, perhaps invariable, properties of our elements other than their combining proportions, their atomic weights, if you please; yet, as far as we know, they approximate more closely than any fixed, if not permanent, ratios. Many of these values, by which we lay such store, are dependent upon data* in which, I venture the assertion, too great confidence has been bestowed, or opinions to which sufficient attention has not been given.

Although in this connection we shall give little heed to the suggested variability of the relative values, it may be remarked that Bouterow, noting the variations observed in 1880 by Schützenberger, who, by the use of different atomic weights, obtained analyses summing 101 instead of 100, expressed the opinion that the chemical value of a constant weight, or rather mass of an element, may vary; that the so-called atomic weight of an element may be simply the carrier of a certain amount of chemical energy which is variable within narrow limits (see also Crookes).

Wurtz's summary of Bouterow's views, at a meeting of the Chemical Society of Paris, provoked an interesting discussion. Cooke later published a statement that he had expressed similar views more than twenty-five years before. That is, in 1855, he had questioned the absolute character of the law of definite proportions, and had suggested that the variability was occasioned by the very weak affinity between elements manifesting a fluctuating composition. Without doubt "The Possible Significance of Changing Atomic Volume," in which a suggestion as to the probable source of the heat of chemical combination is put forward by T. W. Richards, bears directly upon this phase of the problem (*Proc. Am. Acad. Arts and Sciences*, 1901, xxvii., 1, and 1902, xxvii., 399; *CHEMICAL NEWS*, lxxvi., 81).

While the atomic mass values depend directly upon the ratio between the constituents of the compounds, they rest equally upon the molecular weights. Many of the latter attributed to salts of some of the rare earths depend solely upon the specific (*Berichte*, 1880, xiii., 1461) heat determinations of Hillebrand and Norton (*Pogg. Ann.*, 156 *et seq.*), Nilson and Pettersson (*Berichte*, 1880, lxiii., 146), who, in the light of subsequent investigations we know, worked with complexes. To be sure, those elements which were apparently exceptions to the law of Dulong and Petit possess low atomic weights (glucinum, boron, carbon, silicon, aluminum, and sulphur), and have for the most part been brought into harmony. "The specific heats of all substances vary with the temperature at which they are measured; and though the variation is often slight, it is occasionally of relatively great dimensions. When this is so in the case of an element, the question arises:—At what temperature must the measurement of the specific heat be made in order to get numbers comparable with those of the other elements? No definite answer has been given to this question, but it is found that as the temperature rises the specific heat seems to approach a limiting value, and this value is not in general far removed from that which would make the atomic heat approximately equal 6.4 ("Introduction to Physical Chemistry," James Walker, London, p. 33). In view of this allotropism, and the work of Richards adverted to, it appears that a revision of the specific heat values now taken is necessary before we can accept fully this law, which has been most helpful.

Time will not admit of detailed statements, and it is unnecessary in this presence to more than call attention to the fact that what has been said is not applicable to each specific case. "La critique est facile, mais l'art est difficile," as Berthelot ("Les Origines de l'Alchimie," Paris, 1885) has said, yet we must appreciate that all our laws have their limitations. "Man being servant and interpreter of nature can do and understand so much, and so much only, as he has observed in fact or in thought in the course

* Others have been referred to in the Address to which this a sequel (*loc. cit.*).

* Address of the Vice-President of Section C (Chemistry) of the American Association for the Advancement of Science, St. Louis Meeting, December 28, 1922.

of nature. Beyond this he neither knows anything nor can do anything" (Bacon's "Novum Organum," Aphorism I.).

A glance at the extensive, even censored, list of claimants will evoke serious thought. "Thus was the building left ridiculous" (Milton, "Tower of Babel"). The difficulties briefly outlined and the causes for lack in uniformity are by no means insurmountable, but will continue until more systematic direction and prosecution of the work come about. Investigators in pure chemistry as a rule hold professorships, or other positions making equal demand upon their time. Furthermore, it is extremely rare that one man can become a master of the various delicate operations hinted at. Mallet (Stas Memorial Lecture, Chemical Society, London, delivered December 13, 1892) made a proposition for systematising atomic weight work, and F. W. Clarke in this country (Presidential Address before the American Chemical Society) and abroad (Wilde Lecture at the Dalton Centenary, Manchester, 1903) has urged the establishment of an institute for its prosecution. This appeals to all interested in what we are pleased to term the exact sciences, and doubtless in time will come about. For the time being, however, it is not unreasonable to suppose that a concerted appeal of the chemists of this country to the direction of the munificent endowment recently made American science for funds to clarify the elemental enigma presented above would be in vain. There are splendidly equipped chemical departments in some of our great American universities which would make room for, and cordially welcome, I am sure, a selected corps of supported researchers, who would test the claims of each of these and other elemental aspirants. Such a community of effort should receive even greater substantial assistance from governments and corporations than has been accorded individuals. I need only refer to the aid given the Curies by the Austrian government, and generosity shown by the Welsbach Lighting Company in this country to several investigators, especially myself.

It must be evident to all that we are not indulging in special pleading, for every phase of that division of science designated chemistry rests upon what we choose to term the elements.

Victor Meyer, referring to the phantasies of science, said (lecture on "The Chemical Problems of To-day" before the Association of German Naturalists and Physicians at Heidelberg, September, 1889; *CHEMICAL NEWS*, lxi., 21):—"He, however, who only knows chemistry as a tradition of perfectly clear facts, or who thinks to see the real soul of chemical study in measuring physical phenomena which accompany chemical transformations, feels no breath of this enjoyment." Reflecting upon the good and ill that have come to us through unrestrained imagination, we may give a careful acceptance of Newton's "physics, beware of metaphysics," for as Clifford wrote, "Doubtless there shall, by and by, be laws as far transcending those we know as they do the simplest observations."

The graphic representation of the elements, "the foundation stones of the material universe which, amid the wreck of composite matter, remained unbroken and unworn," as Maxwell gracefully spoke of them, has often been mistaken for the periodic law. Carnelley's "reasonable explanations" of the periodic law were given a respectful hearing and forgotten.*

"Granting that the chemical characteristics of an element are connected with its atomic weight, we have, however, no right to assume them to be dependent upon that fact alone" (Livinge). Hinrichs ("Atom Mechanics," vol. i., p. 242, St. Louis, 1894) says weight and form, concerning the latter of which I am ignorant. No doubt the pendulum lately has swung back toward Berzelian thought revived by the like masters, van 't Hoff and Arrhenius.

Le Verrier predicted the planet Neptune, and his predictions were verified. While all of Mendeleeff's predictions, specific and tacit, have not been verified, some have. Ramsay (Address before the Chemical Section, British Association, Toronto Meeting, 1898) and others, without a periodic guide, predicted certain of the inert gases, which predictions have been verified.

Victor Meyer, in speaking of the completion of the Mendeleeff table, calls attention to the summing up of one hundred elements, from which it appears that 258 would be the limit to our atomic mass equivalents. I am not prepared positively to contradict such a conclusion at the present time, but there are reasons for thinking otherwise.

Clarke has shown that the mean density of the earth, 5.5 to 5.6, is more than double that of the rocky crust, and "the difference may be accounted for as a result of pressure, or by supposing that, as the globe cooled, the heavier elements accumulated towards the centre" ("The Relative Abundance of the Chemical Elements," F. W. Clarke, read before the Philosophical Society of Washington, October 26, 1899; *CHEMICAL NEWS*, lxxii., 31). While it is quite impossible to judge of the order of this intramundane pressure, I am not aware of such marked changes being brought about in the specific gravities of the heavier solid elements or their compounds either by pressure, allotropic or isomeric changes, except the cerebral argentaureum of the late S. H. Emmens (Argentaureum Papers published by Emmens, New York). The examinations of volcanic dusts by Hartley (Royal Society, February 21, 1901; *CHEMICAL NEWS*, lxxxiii., 174), Fleet (*Abstr. Proc. Geol. Soc.*, 1902, 117; *Journ. Chem. Soc.*, 1902, lxxxi.—lxxxii., [2], 518) and others appear to contradict the latter explanation, although we are unable to state the depth, perhaps within the shell considered by Clarke, at which volcanoes begin their boisterous activity. While awaiting a fulfilment of Martinez' ("La Nature," *Sc. Am. Sup.*, 1886, xxi., 546) project to explore the earth's centre, we may offer a third solution, not wholly unscientific, as it can do no harm, and has ought to do with any yellow peril in science, namely, the existence of elements with atomic weights higher than those set by the silent limit of periodic tables.

"Most molecules—probably all—are wrecked by intense heat, or, in other words, by intense vibratory motion, and many are wrecked by a very impure heat of the proper quality. Indeed, a weak force, which bears a considerable relation to the construction of the molecule, can by timely savings and accumulation accomplish what a strong force out of relation fails to achieve" (Tyndall in *Longman's Magazine*).

As hinted at in the earlier portion of this unconsciously prolonged address, many have theorised as to the ultimate composition of matter. The logic of Larmor's theory (*Phil. Mag.*, 1897, 506), involving the idea of an ionic substratum of matter, the support of J. J. Thomson's experiments (*Phil. Mag.*, October, 1897, 312), the confirmation of Zeeman's phenomenon, the emanations of Rutherford, Martin's explanations (*CHEMICAL NEWS*, 1902, lxxxv., 205), cannot fail to cause credence in the correctness of Crookes's idea of a fourth state of Matter (*Phil. Trans.*, 1881, ii., 433). In the inaugural address as President of the British Association, 1898, he acknowledges in the mechanical construction of the Röntgen ray tubes a suggestion by Silvanus Thompson to use for the anti-cathode a metal of high atomic weight. Osmium and iridium were used, thorium tried, and in 1896 Crookes obtained better results with metallic uranium than platinum.

These and the facts that most of the elements with high atomic weights, in fact all above 200 (thallium not reported on), exhibit radio-active properties, are doubtless closely associated, and have to do with the eventual composition of matter. I have unverified observations which go to show the existence of at least one element with a very high atomic weight. If it be confirmed, then we have them now or they are making, and probably breaking up, as shown by that marvellous class of elements in the discovery of which the Curies have been pioneers.

* He regarded the elements as compounds of carbon and other analogous to the hydrocarbon radicals, and suggested that all known bodies are made up of three primary elements—carbon, hydrogen, and ether—truly an assumption which cannot be disproved. Aberdeen Meeting, British Association.

During 1881 and 1882, he had constructed in his laboratory in the Boulevard Berthier, an apparatus with three concentric vessels 1·5 metres high and 0·75 metre in diameter. A six-horse-power gas-engine drove the compression pumps, and the temperature fell rapidly in the central portion of the apparatus to 85° below zero. It would require the resources of a factory and a large outlay of capital to obtain better returns than from this freezing machine. It is to be regretted that the plans were never published, as they anticipated the tubular apparatus now in use. I think with regret of the disappearance of a piece of apparatus that would now hold such an interesting place in the history of the liquefaction of gases. Though it could be foreseen already that it would be possible to approach very close to absolute zero, Demarcq gave up the research that he could only attempt with means that appeared to him to be too feeble. Seeking always for the essential relations that might exist between physical forces and chemical material, he organised the finest apparatus for producing vacua in Paris. By means of various

systems of mercury-falls, the vacuum became sufficiently good for the carrying out of conclusive experiments. In 1883, an interesting summary of observations appeared on the volatility of zinc, cadmium, and gold in the cold. It was shown that matters which appeared fixed to us is slowly dissipated *in vacuo*, and without doubt, though with diminished speed, they are all volatile at the ordinary atmospheric pressure.

Following up his inquiries on physical questions, Demarcay proposed to examine the variations of the spark spectra at the highest temperatures then attainable. With this object he constructed a coil with a short secondary wire of large diameter, giving very intense, globular, luminous, and hot sparks. These sparks have all the characteristics in spectroscopic practice of a small arc passing between poles of pure metals of different kinds, or, in the case of saline solutions, between two poles of pure platinum. Such an arrangement limits the lines foreign to the substance under examination to the known spectrum of the pure platinum wire serving as the electrodes.

It is with this apparatus that M. Demarcay instituted the method of separation of the rare earths. In 1900, the Parisian firm of Chénal and Douillet exhibited a collection of enormous crystals of pure salts of neodymium, praseodymium, samarium, &c., obtained by closely following Demarcay's instructions, and this caused considerable astonishment among certain specialist chemists throughout the world, who had written much on the subject, and some of whom had exhibited pasty masses devoid of any well defined colour.

In the separation of the very closely allied rare earths, Demarcay practised fractionation like all the other chemists, but he knew how to do it. The following is a brief summary of his method:—The salts of the numerous rare earths are fractionated in aqueous solution, and it matters little what salt is used, so long as it is relatively slightly soluble, as is the case with the double salts. At first the separations proceed, and we have every reason to believe that the only good method has been found. This state of affairs must be utilised to isolate that portion which goes best. Soon the best conducted work shows no further progress. It is no use revolving against nature; the work is stopped; spectrum analysis has shown that traces of salts, other than those we wish to separate, have accumulated in the fractions which no longer advanced; these are calcium and yttrium. Everything is stopped until these interfering elements have been got rid of by known means; then we again make the double salt on which the fractionation in aqueous solution had been previously carried out as if nothing had intervened, and the separation again gives good results. However, a time comes, in spite of everything, when the separation ceases, a state of equilibrium has been produced which cannot be upset. The salts of the rare earths, and the accompanying salt and the water, have become arranged naturally into unchangeable proportions. It is necessary to destroy this equilibrium, either by continuing the fractionation in aqueous solution but changing the accompanying salt, or by changing the nature of the solvent. It was in this latter manner that Demarcay, whose method I have only described summarily, often fractionated in fuming nitric acid instead of water, making use of nitrate of magnesium as the adjuvant salt. He also used with advantage a medium composed of the double sulphates of the rare earths with rubidium.

In this kind of work, too briefly described, our lamented *confère* knew how to seize the right moment, and in this he was an artist in science. In all that is most elevated science teaches manipulation to its workers through the conception of philosophy and the vision of art.

Proceeding on this idea, Demarcay himself only undertook the most difficult fractionations. He succeeded in discovering an element most extremely rare in nature, europium, and would soon have fixed the individuality of this principal body which figures in what we call "erbium," if death had not removed him.

The laboratory where Demarcay worked was one of great renown. There, and there only, a complicated spectrum was read like an open book. Everyone who thought he had found a new pure element took it to Demarcay and was immediately enlightened. One of our eminent physicists, M. Curie, had a parcel of salts of barium examined in this manner at the commencement of his research on radium, and in which M. Demarcay immediately observed a line he did not recognise.

To-day, savants feel keenly the void left by the only man who could inform them with certainty as to the nature and purity of an element, or on the neglected residues of a new mineral.

Demarcay foresaw his own approaching death, but was conscious of a duty performed, and grateful for the years he had lived. He asked for no further reward than that felt by a keen intelligence when it gives rise to a flash of thought that will be remembered throughout the world.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 4.

ON THE RESISTANCE OF IRIDIO-PLATINUM ANODES USED IN THE ELECTROLYSIS OF ALKALINE CHLORIDES.

By P. DENSO.

HABER (*Zeit. für Anorg. Chem.*, 1898, vol. xvi., p. 438) effected the electrolysis of hydrochloric acid of different concentrations and at different temperatures with electrodes of platinum and iridio-platinum, and he found that the anodes containing from 10 to 25 per cent of iridium were not attacked.

It became of interest to see if anodes in the form of very thin sheets could be employed with advantage in the electrolysis of the alkaline chlorides. With electrodes of such thinness the cost would be considerably reduced, and if they were sufficiently resisting they might, in certain cases, replace carbon electrodes. The results of the experiments agree with those obtained by Haber.

The experiments were carried out by means of a series of electrodes of iridio-platinum of two different sizes, and containing from 7.6 to 15 per cent of iridium. They had a thickness of only 0.007 m.m., and were soldered to a wire of the same metal 1 m.m. in diameter. The large electrodes were 40 m.m. wide and 125 m.m. long, and consequently had a total surface area of 1 square decimetre; the small electrodes were 20 m.m. wide and 125 m.m. long, and had an area of 0.5 square decimetre.

The electrodes described above were used for the electrolysis of alkaline chlorides under various conditions; for instance:—

The electrolysis of a concentrated solution of chloride of potassium at 20° without a diaphragm.

The electrolysis of a concentrated solution of chloride of potassium at 80° without a diaphragm. (These solutions of chloride of potassium were treated with 2 per cent of chromate of potassium.)

The electrolysis of a concentrated solution of chloride of sodium at 20° with a diaphragm.

The electrolysis of a concentrated solution of chloride of sodium at 80° with a diaphragm.

In the electrolysis of solutions of chloride of sodium, the anodes were placed in a large volume of liquid, about 7 litres.

After these experiments were finished we passed to the electrolysis of hydrochloric acid at 20 per cent at a temperature of 80°, as the chlorine given off by hydrochloric acid has a more energetic action on iridio-platinum than that given off by solutions of the chlorides. In these experiments the anode under examination was placed between two cathodes.

The results of all these experiments are given in the accompanying table.

No.	Electrode.	Electrolyte.	Current.	Weights of electrodes.	
				Grams.	Grm.
1.	10 per cent iridium. O = 1 sq. decim.	Chloride of potassium, without diaphragm. T = 20—50°.	I = 10.5 d = 10.5	At first 4.8745 After 800 a.-h. 4.8741	Diminution 0.0004
2.	10 per cent iridium. O = 1 sq. decim.	Chloride of potassium, without diaphragm. T = 80°.	I = 30 d = 30	At first 6.7705 After 1200 a.-h. 6.7700	Diminution 0.0005
3.	10 per cent iridium. O = 1 sq. decim.	Chloride of sodium, with diaphragm. T = 20°.	I = 10 d = 10	At first 8.4525 After 240 a.-h. 8.4525	Diminution 0.0000
4.	9.5 per cent iridium. O = 1.2 sq. decim.	Chloride of sodium, with diaphragm. T = 80°.	I = 20 d = 16.7	At first 9.8910 After 200 a.-h. 9.8875 " 400 " 9.8871	Diminution 0.00035 Further diminution 0.00004
5.	7.63 per cent iridium. O = 0.5 sq. decim.	HCl, 20 per cent. T = 80°.	I = 10 d = 20	At first 5.4061 After 70 a.-h. 5.4051 " 140 " 5.4044 " 210 " 5.4044	Diminution 0.00010 Further diminution 0.00007 0.00000
6.	9.5 per cent iridium. O = 0.5 sq. decim.	HCl, 20 per cent. T = 80°.	I = 5 d = 10	At first 5.0588 After 10 a.-h. 5.0550 " 50 " 5.0554 " 80 " 5.0550	Diminution 0.00029 Further diminution 0.00007 0.00002
7.	9.5 per cent iridium. O = 0.5 sq. decim.	HCl, 20 per cent. T = 80°.	I = 10 d = 20	At first 5.6620 After 10 a.-h. 5.6620 " 35 " 5.6620 " 90 " 5.6620	Diminution 0.00000 Further diminution 0.00000 0.00000
8.	0.888 per cent iridium. O = 0.5 sq. decim.	HCl, 20 per cent. T = 80°.	I = 10 d = 20	At first 5.3367 After 70 a.-h. 5.3360 " 140 " 5.3360	Diminution 0.00007 Further diminution 0.00000
9.	15.05 per cent iridium. O = 0.5 sq. decim.	HCl, 20 per cent. T = 80°.	I = 10 d = 20	At first 5.3700 After 70 a.-h. 5.3695 " 140 " 5.3660 " 200 " 5.3658	Diminution 0.00005 Further diminution 0.00005 0.00002

The surface O means the total surface of the anodes. I represents the current in amperes; d the density of the current per square decimetre. The computation of the ampère-hours, a.-h., was made, with the exception of Experiment 1, with a copper voltmeter by multiplying the constant current I by the length of time measured accurately. T represents the temperature of the electrolyte. The different alloys of platinum and iridium used were made by W. C. Heraeus, and then analysed. In Experiments 1 and 3 we used the same electrode, and, beginning with Experiment 4, a fresh electrode was used every time. The cathodic solution in Experiment 4 was renewed every hour with a fresh concentrated solution of chloride of sodium.

Experiment 7.—Before being used the electrode was plunged into concentrated hydrochloric acid for fifteen hours, and there was no diminution of weight.

Experiment 8.—The electrode contained 9.88 per cent of commercially pure iridium, the others contained very pure iridium, and no sensible difference could be found in these two kinds of material. The first kind of electrode contains Rh, Ru, Fe, and Cu in much greater quantity than the second; still these are low in both cases, and the experiments do not show any difference; see Mylius and Förster on the preparation of pure platinum, *Berichte*, vol. xxv., p. 665.

Experiment 9.—The electrode experienced a considerable diminution in weight, 0.0035 grm., after the second experiment with 70 ampère-hours; this can be explained by the formation of small holes in the electrode, proving its non-homogeneity. Apart from this defect, this electrode behaved like the others.

Experiments 1 and 3 showed that the electrodes used are very resistant to chemical action, as will be seen from the experiments with hydrochloric acid at 20 per cent, and 80°.

Further, it has been observed that with electrodes containing 7.5 to 15 per cent of iridium there was no sensible difference.

To sum up, electrodes of iridio-platinum of 0.007 m.m. in thickness are very resistant to the electrolysis of alkaline chlorides, and their use in ordinary practice can be recommended without hesitation.—*Zeitschrift für Elektrochemie*, vol. viii., p. 147.

The Use of Organo-magnesian Compounds in Analytical Operations.—L. A. Tchougæff. —The organo-magnesian compounds discovered by Grignard, which are of such value in organic synthesis, may be of great use in analytical determinations. We know that the magnesian compounds of the type RMgI decompose water according to the following equation:— $\text{RMgI} + \text{H}_2\text{O} = \text{RH} + \text{MgIOH}$. Other hydroxylised compounds, such as the alcohols, phenols, and oximes (without mentioning the acids) give an analogous reaction: $\text{RMgI} + \text{R}_1\text{OH} = \text{RH} + \text{R}_1\text{OMgI}$. This property may be utilised for a double purpose:—1. As a means for the diagnosis of the hydroxylised compounds. These latter, properly dried, are brought into contact with an excess of the methyl-derivative, CH_3MgI . The reaction can be brought about in a Knop apparatus; the disengagement of methane will indicate the presence of the CH group. 2. As a means for the separation of substances containing hydroxyl from those which do not contain it—for example, for the separation of the alcohols from the hydrocarbides. To the mixture in question we add a slight excess of CH_3MgI in ethereal solution; CH_4 is given off, and the alcohol passes into the non-volatile form of combination, ROMgI . The carbide is not changed; it can now be separated by distillation under reduced pressure, after evaporating off the ether, and from the residue the alcohol can be re-formed by the action of water on the ROMgI . In this manner the author has already obtained several results of practical utility, and is continuing his researches.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 652.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 3rd, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. W. W. Underhill and J. A. Goodson were formally admitted Fellows of the Society.

The PRESIDENT announced that arrangements had been made for the delivery of a Faraday Lecture this year. The invitation addressed in the first instance to Professor Emil Fischer had been accepted and a date in November last had been selected for the lecture, but to the great regret of the Council the state of Professor Fischer's health had prevented him from fulfilling his engagement. Professor Ostwald, of Leipzig, had, however, been good enough to accept an invitation to give the lecture on April 19th next, and by the courtesy of the authorities of the Royal Institution the discourse would be delivered in the Theatre of that Institution. Arrangements as to the admission of Fellows of the Society would be announced later in the *Proceedings*.

Certificates were read for the first time in favour of Messrs. Robert S. Finlow, Pemberandah, Dalsingh Serai, India; Robert de J. Fleming-Struthers, B.A., Exeter College, Oxford; George Mathieson Horn, Ivylands, Epping; Alfred Mander, Berkswell, Malvern; Gerald Pinchbeck, 66, Albany Street, Regent's Park, N.W.; Walter Tong, Pole Lane, Failsforth, Manchester.

Of the following papers, those marked * were read:—

*33. "Chemical Dynamics of the Alkyl Iodides." By MISS KATHERINE B. BURKE and FREDERICK GEORGE DONNAN.

The reactions between silver nitrate and certain of the alkyl iodides in absolute alcoholic solutions were shown to be very complicated, and the main conclusions deduced are summarised as follows:—

1. The reactions between silver nitrate and an alkyl iodide in absolute alcohol at 24.5° and at concentrations varying from N/20 to N/80 can be expressed by a special form of the bimolecular velocity-equation, in which the velocity-coefficient is a function of the initial concentration of the reacting components.

2. It is found that in solutions containing the reagents in equivalent amounts, the velocity-coefficient (k) increases as the initial molecular concentration (c) increases, the relation between k and c being $k = Kc^{0.53}$; where K is independent of concentration.

3. This variation of k is chiefly due to the silver nitrate. For solutions containing the same (N/40) initial concentration of ethyl iodide and varying (N/20—N/80) initial concentration (c) of silver nitrate, the relation between k and the latter is approximately $k = Kc^{\frac{1}{2}}$. For solutions containing the same initial concentration of silver nitrate and varying initial concentration of ethyl iodide, the value of k decreases as the latter increases, but the rate of decrease is relatively small as compared with the rate of increase produced by silver nitrate.

4. It has not been found possible to explain the variations of k indicated in 1, 2, and 3. In particular, the assumption that it is the silver ions which take part in the fundamental reaction which regulates the speed does not appear to offer a simple explanation.

5. Similar anomalies have been observed by Hecht, Conrad, and Brückner in the case of ether-formation from sodium alkylxide and alkyl iodide in alcoholic solution, but the explanation of these anomalies proposed by Steger, based on assumptions concerning the ionisation of the sodium alkylxide in alcoholic solution, does not appear to be valid if the ordinary law of equilibrium is assumed.

6. The theory of "alkylene" and "alkylidene" dissociation of the alkyl iodides, proposed by Nef, does not give a satisfactory account of the observed results.

7. As stated by Nef, nitric acid is the only acid produced in the reaction. Chiminello's statement that acetic acid is formed appears to be incorrect. The other products of the reaction are ether and alkyl nitrate.

8. If the reactivities of the alkyl iodides are measured by the velocity-coefficients of the reaction with silver nitrate in absolute alcohol (N/40 equivalent solutions at 24.5°), the order of reactivity (beginning with the greatest) is isopropyl, ethyl, *n*-propyl, methyl, *n*-butyl, isooctyl, isobutyl.

9. This order of reactivities corresponds with the rate of production of free iodine in the alcoholic solutions when exposed to air and light, with the single exception of methyl iodide, the solution of which becomes discoloured at a rate between those of solutions of isopropyl and ethyl iodides.

10. The relative reactivities referred to in 8 do not agree in many respects with those observed in other reactions which have been studied kinetically, such as the reactions with ethyl sodioacetate, triethylamine, sodium alkylxide. Compared with these results, isopropyl iodide reacts with abnormally great, and methyl iodide with abnormally small velocity. It does not appear possible, therefore, to ascribe the reactivity of the alkyl haloids to any uniform cause (such, for example, as a dissociation, whether "alkylidene," "alkylene," or electrolytic).

11. So far as the final products and not the kinetics of the reaction are concerned, the production of ether and nitric acid can be explained by ionic reactions just as well as by Nef's hypothesis.

*34. "Separation of β -Crotonic Acid from α -Crotonic Acid." By ROBERT SELBY MORRELL and ALBERT ERNEST BELLARS.

The separation of β -crotonic acid from α -crotonic acid was formerly effected by means of the different solubilities of the sodium salts in alcohol (Michael and Schulthes, *Journ. Pr. Chem.*, 1892, [2], xlv., 245), the β -crotonate being more soluble in absolute alcohol than its α -isomeride. The α -crotonic acid thus obtained was considered by J. Wislicenus to be not entirely free from the α -acid (*Chem. Centr.*, 1897, ii., 259).

The salts of β -crotonic acid with brucine and quinine have been found to be less soluble than the corresponding derivatives of α -crotonic acid. The brucine salts are unfortunately very soluble in most solvents, but the quinine salts are very sparingly soluble in water, and it is easy to separate quinine β -crotonate (m. p. 157°) from quinine α -crotonate (m. p. 134°) by fractional crystallisation; the solubility of the β -crotonate in water at 17° is 1.0, whilst that of the α -crotonate is 2.4 at the same temperature, and two crystallisations are sufficient to complete the separation.

The barium β -crotonate, $\text{Ba}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot \text{H}_2\text{O}$, obtained from the quinine salt, when suspended in pure ether and decomposed by dilute sulphuric acid, yielded the pure β -crotonic acid (m. p. 15°, sp. gr. 1.0342 at 12.5°). Its physical and chemical properties agree with those described by Michael and by J. Wislicenus (*loc. cit.*). The molecular weight in glacial acetic acid is 85.6, and the molecular refraction is 37.2.

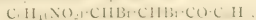
The advantage of the following method of separation lies in the fact that fractional distillation of the two acids is avoided, and it is easier to obtain the less soluble quinine β -crotonate in a pure state than to remove sodium α -crotonate completely from the more soluble sodium β -crotonate.

*35. "Contributions to the Knowledge of the β -Diketones." By SIEGFRIED RUHEMANN and EDWIN ROY WATSON.

The authors have repeated Wislicenus's experiments on the action of alcoholic potash in benzylideneacetophenone dibromide, and find that the compound produced has the empirical formula $\text{C}_{17}\text{H}_{16}\text{O}_2$, and not $\text{C}_{15}\text{H}_{12}\text{O}_2$, as stated by Wislicenus (*Annalen*, 1899, cccviii., 219), and that it is the ethyl ether of dibenzoylmethane, $\text{C}_6\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_5) : \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$. Under the influence of

hydrochloric acid, the substance decomposes into ethyl chloride, acetophenone, and benzoic acid.

Alcoholic potash behaves similarly towards the dibromide of β -nitrobenzylideneacetophenone.



yielding the ethyl ether of β -nitrodibenzoylmethane, $\text{C}_6\text{H}_5(\text{NO}_2) \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_5) \cdot \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ (m. p. $80-81^\circ$).

The authors have also examined the action of ammonia and organic bases on the olefinic diketones. Thus benzylideneacetylacetone reacts with aniline to form the compound $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_5) \cdot \text{CH}(\text{CO} \cdot \text{CH}_3)_2$ (m. p. 113°). This, on heating, decomposes into benzylideneaniline and acetylacetone. Phenylhydrazine reacts with benzylideneacetylacetone and also with benzylidenebenzoylaceton with evolution of heat. The additive compounds could not be obtained, since, in each case, they are decomposed at once with the formation of benzaldehyde phenylhydrazine.

With benzylideneacetylacetone, alcoholic ammonia forms the compound $\text{C}_{10}\text{H}_{15}\text{ON}_2$ (m. p. 147°), which is to be regarded as acetyldiphenylmethyltetrahydropyrimidine, $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{C}(\text{NH} \cdot \text{CH}_2\text{C}_6\text{H}_5)_2 \cdot \text{NH}_2$.

The diketones react with semicarbazide with the elimination of 1 molecule of water and the formation of $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}_3$ (m. p. 210° with decomposition) and $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}_3$ (decomposing at 230°). These compounds may be regarded as semicarbazones, but taking into consideration the behaviour of other bases towards the diketones, the alternative view of representing them as cyclic compounds cannot be disregarded.

The additive compound obtained from benzamide and benzylidenebenzoylaceton (*Trans.*, 1903, lxxiii., 1372) may also be regarded as being formed by the addition of the base to the ethylenic linking of the olefinic ketone.

*36. "The Purification of Water by continuous Fractional Distillation." By WILLIAM ROBERT BOUSFIELD.

An apparatus was described in which water is distilled continuously from a copper boiler, freed from spray by means of a system of baffle plates, and condensed on surfaces kept at different temperatures by an adjustable supply of cold water. The hottest surfaces yield distilled water of ordinary quality, whilst the coldest surfaces give water of conductivity 1 to 2 reciprocal megohms per c.c., which is sufficiently pure for the majority of conductivity measurements, and contains only a small proportion of ammonia.

*37. "Freezing-point Curves of Dynamic Isomerides. Ammonium Thiocyanate and Thiocarbamide." By ALEXANDER FINDLAY.

The author has studied the equilibrium relations of the dynamic isomerides, ammonium thiocyanate, and thiocarbamide from the point of view of the phase rule, attention being directed chiefly to the determination of the freezing-points of mixtures of these substances with the view of ascertaining what compounds, if any, are formed at temperatures in the neighbourhood of the freezing-points, and the conditions of their stability (compare Emerson Reynolds and Werner, *Trans.*, 1903, lxxiii., 1). The freezing-point curve obtained is of the simplest form, consisting of two branches meeting at a eutectic point which lies about 104.3° . The melting-points of ammonium thiocyanate and of thiocarbamide can be determined only approximately on account of the occurrence of isomeric transformation. The melting-point of ammonium thiocyanate may be taken as being about 149° and that of thiocarbamide as not lower than $175-177^\circ$, these being determined by comparison with camphor. The natural freezing-point is $114-115^\circ$, the stable form being ammonium thiocyanate. From the simple form of the freezing-point curve obtained, it follows that no compound is formed which is stable at the temperatures indicated on this curve. This conclusion is supported by the form of the cooling curve and by the analysis of the solid phase.

From the fact that the equilibrium-point in the liquid phase is independent of the temperature, it follows that the

isomeric transformation is not accompanied by any heat effect.

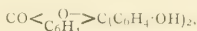
38. "The Constitution of Phenolphthalein." By ARTHUR GEORGE GREEN and ARTHUR GEORGE PERKIN.

The authors have found that a solution of phenolphthalein, decolorised by an excess of caustic alkali, can be entirely neutralised without any return of the colour taking place, by careful titration at a low temperature with dilute acetic acid. If, however, the colourless neutral solution is boiled, the red colour returns in its full intensity, whilst at the same time the solution becomes alkaline. If the solution is acidified and either left for some time or heated, a precipitation of free phenolphthalein occurs, which also dissolves in aqueous alkalis to a red solution. The point at which neutrality occurs in the titration with acetic acid corresponds with the presence in the colourless solution of the carbinolcarboxylic acid salt, $\text{C}_6\text{H}_4(\text{CO}_2\text{M}) \cdot \text{C}(\text{OH})(\text{C}_6\text{H}_5)_2 \cdot \text{OH}$.

These observations do not agree with the electrolytic dissociation hypothesis, but are simply explained by the quinonoid theory if the colour changes are attributed to a variation of type from a quinonoid to a benzenoid form and *vice versa*, due to hydration and dehydration.

Thus, the first action of an alkali on the free phenolphthalein (lactone) would probably be the replacement of the phenolic hydrogen by the alkali metal. This salt being unstable may be supposed to undergo immediate transformation into the coloured quinonoid salt, $\text{C}_6\text{H}_4(\text{CO}_2\text{K}) \cdot \text{C}(\text{C}_6\text{H}_5)_2 \cdot \text{O}$, by direct transference of the metal from the phenolic to the carboxylic group.

With excess of caustic alkali, this coloured salt is converted, by assumption of KOH, into the colourless carbinol salt, $\text{C}_6\text{H}_4(\text{CO}_2\text{K}) \cdot \text{C}(\text{OH})(\text{C}_6\text{H}_5)_2 \cdot \text{C}_6\text{H}_5 \cdot \text{OK}$, and this product, when neutralised with acetic acid, gives $\text{C}_6\text{H}_4(\text{CO}_2\text{K}) \cdot \text{C}(\text{C}_6\text{H}_5)_2 \cdot \text{OH}$, which is also colourless. Caustic potash is set free on boiling the latter salt, and the lactone,—



which is produced is simultaneously converted into the coloured quinonoid salt by the liberated alkali.

A similar explanation is offered in the case of quinolphthalein, the behaviour of which is found to be exactly similar to that of phenolphthalein.

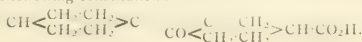
39. "8-Ketohexahydrobenzoic Acid." By WILLIAM HENRY PERKIN, jun.

Ethyl 7-cyanopentane-2,7-tricarboxylate,—



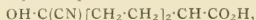
is readily prepared by the interaction of ethyl 3-iodopropionate with the sodium compound of ethyl cyanoacetate; it boils at 228° under 20 m.m. pressure, and, on hydrolysis with hydrochloric acid, yields pentane-2,7-tricarboxylic acid, $\text{CO}_2\text{H} \cdot \text{CH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$ (compare Emery, *Ber.*, 1891, xxiv., 384; Bottomley and Perkin, *Trans.*, 1900, lxxvii., 299). On digesting this acid with acetic anhydride and distilling the product under diminished pressure, water and carbon dioxide are eliminated and 8-ketohexahydrobenzoic acid (cyclohexanone-4-carboxylic acid) is produced, which crystallises with one molecule of water, melts at 68° , and distils at $210^\circ/30$ m.m. It was further characterised by means of its oxime, semicarbazone, and methyl and ethyl esters.

The ketonic acid forms an oily phenylhydrazone, which, on heating with hydrochloric acid, yields tetrahydrocarbazole-p-carboxylic acid (m. p. 195°); compare Baeyer and Tutein, *Ber.*, 1899, xxii., 2184). 8-Ketohexahydrobenzoic acid, when digested with methyl alcohol and sulphuric acid, yields ethyl carboxyhexamethylenyl-8-ketohexahydrobenzoate (b. p. $255^\circ/20$ m.m.). This ester, on hydrolysis, yields the acid, which melts at 170° , and has the following constitution:—



trans-Hydroxyhexahydrobenzoic acid, produced by reducing δ -ketohexahydrobenzoic acid, melts at 121° , and, when heated with hydrobromic acid, is converted into trans- δ -bromohexahydrobenzoic acid, (bromocyclohexane-4-carboxylic acid) (m. p. 167°), and this, when digested with sodium carbonate, loses hydrogen bromide, yielding Δ^3 -tetrahydrobenzoic acid, which melts at about 13° and distils at 237° 748 m.m.; it combines with hydrobromic acid to form γ -bromo- α -hydrobenzoic acid, (m. p. 122°), and also absorbs bromine at the ordinary temperature, yielding γ - δ -dibromo- α -hydrobenzoic acid (m. p. 86°).

δ -Ketohexahydrobenzoic acid combines with hydrogen cyanide, and from the product, the nitrile of trans- α -hydroxy- α -hydrotetrephthalic acid,—



was isolated in the form of pale yellow crystals melting at about 140° . This nitrile yields, on hydrolysis, trans- α -hydroxyhexahydrotetrephthalic acid (m. p. 228 – 230°). If the crude product of the action of hydrogen cyanide on ketohexahydrobenzoic acid is hydrolysed, the principal product obtained is α -hydroxyhexahydrotetrephthalic acid, (m. p. 168 – 170°).

Both *cis*- and *trans*-hydroxy-acids are decomposed on distillation, with loss of water and formation of Δ^1 -tetrahydrotetrephthalic acid (Baeyer, *Annalen*, 1888, cxlv., 160).

The investigation of δ -ketohexahydrobenzoic acid is being continued.

(To be continued.)

NOTICES OF BOOKS

The Grant and Validity of British Patents for Inventions.

By JAMES ROBERTS, M.A., LL.B., &c. With many Diagrams. London: John Murray. 1903. Pp. 647.

It has been said that the granting of a patent gives the inventor no privilege beyond that of defending its validity in a court of law. This is perhaps rather overstating the case, still it must be admitted that the English Patent Law is in a very unsatisfactory condition. We find it stated in this volume that no fewer than 42 per cent, or about 5780 patents granted per annum in England, are invalid on the ground of having been already patented in this country. An examination of the results of litigation shows that no less than 51 per cent of those patents which are commercially worth infringing are invalid; thus about £23,120 per annum is paid for patents which give no legal protection to the patentees.

A new procedure is about to be introduced which will prevent the granting of a large proportion of bad patents. Under this new procedure, questions of alleged anticipation will arise, and these questions will have to be considered by the inventor before, instead of as heretofore after the grant is made.

This work, which is divided into three principal parts, deals with the subject up to the grant of the patent and the amendment of specifications, and is of necessity a law book.

Part I. deals with the general principles and rules affecting the grant and validity of patents, and contains nine chapters.

Part II. consists of abstracts of leading and illustrative cases with notes; this part covers nearly 300 pages, and illustrates the application of the principles in Part I.

Part III. deals with the statutes and rules, in so far as they bear on the grant of patents.

It is stated by the author that the book has been written for inventors, but we can hardly believe that many inventors would take the trouble to consult it; moreover, if they did they would probably not be able to follow it. As we remarked above, it is essentially a law book, and as such will no doubt be of great service to patent agents and practising lawyers, who make a speciality of this particular branch of their profession.

Drugs, their Production, Preparation, and Properties. By H. WIPPELL GADD, F.C.S. &c. London: Baillière, Tindall, and Cox. 1904. Pp. 180.

ALTHOUGH this book has been written primarily for students, it will also be found useful by others who occasionally need information, or wish to refresh their memories concerning medicinal products. It embraces all the drugs included in the Pharmacopoeia, and they have been arranged in classes, like being placed with like.

The book is divided into three sections, dealing respectively with (1) vegetable, (2) animal, and (3) chemical products, and is provided with a good index and table of contents.

Dispensing made Easy: with numerous Formulae, and Practical Hints to secure Simplicity, Rapidity, and Economy. By WM. G. SUTHERLAND, M.B. (Aberd.). Bristol: John Wright and Co. 1904. Pp. 102.

IN most aids to dispensing a good deal of space is taken up with such subjects as pill-rolling, pill-coating, the making of emulsions, &c., subjects in which the dispensing medical practitioner takes little or no interest. The present volume has been compiled with the object of rendering dispensing as easy as possible, especially to those who have a large club, colliery, or works practice. Economy as well as rapidity is necessary in a practice of the kind just mentioned, and many a useful hint in this direction will be found in these pages.

The Cyanide Process of Gold Extraction. A Text-book for the Use of Mining Students, Metallurgists, and Cyanide Operators. By JAMES PARK, Professor of Mining and Director of Otago University School of Mines. Third English Edition, Revised and Enlarged. With Frontispiece, Plates, and Illustrations. London: Charles Griffin and Co., Ltd. 1904. Pp. 193.

THE rapid succession of new editions of this book bear ample evidence as to its value; the first English edition was only published in 1900, and we have already to do with the third.

In this edition much new material has been added, for the most part relating to the lead-smelting of gold slimes, the treatment of sulpho-telluride ores, and filter-press practice.

The value of filter-pressing of course varies with the different gold-fields. In Western Australia its adoption was mainly determined by a combination of local conditions; tendency of the ores to form slimes, the scarcity of fresh water, and the saline character of the only water available for milling; these slimes were of high value. On the other hand, in South Africa the mill-slimes are only a secondary consideration, and are of low grade.

The adoption of lead-smelting for gold-slimes is a notable advance in cyanide practice; it is best described as scorification on a large scale, for the reason that the zinc-slimes are melted and the gold recovered in lead bullion; this is then cupelled, or rather, refined. It is claimed that lead-smelting recovers a larger amount of gold than the sulphuric acid method, and in six trials the lead process gave 10.5 per cent higher recovery than the acid treatment.

With regard to the cyanide process as a whole, it has been more largely adopted in the Witwatersrand goldfields than anywhere else. The ore is principally a pyritic silicious quartz conglomerate, and the gold is disseminated throughout the matrix or in the iron pyrites; hence the cyanide process is the most suitable one for its recovery.

In some goldfields, notably the Kalgoorlie, sulpho-telluride ores are met with in large quantities; this requires a modification of the cyanide process, such as the use of cyanogen bromide, &c., the merits of which have been already discussed in these columns.

We can confidently recommend this book as a thoroughly practical work, and congratulate the author on its continued success.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Notes.—All figures of temperature are Centigrade, unless otherwise expressed.

Comptes Rendus Hebdomadaires des Sciences, de l'Académie des Sciences. Vol. cxxxviii, No. 7, February 15, 1904.

Action of Reduced Nickel on the Halogen Derivatives of the Fatty Series in presence of Hydrogen.—Paul. Sabatier and Alph. Mailhe. —A series of experiments on the action of reduced nickel in presence of hydrogen on halogen derivatives of the fatty series show that the halogen is in every case more or less easily eliminated in the form of hydric acid, but it is never replaced by the hydrogen, as is the case in the aromatic series. The result is either the formation of an incomplete compound or the complete destruction of the molecule.

Influence of Complex Ions in Electrolysis by Alternating Currents.—André Brochet and Joseph Petit. —In a previous research the authors proved that the formation of a complex ion is not the true cause of the solution of copper in potassium cyanide under the influence of an alternating current. They now consider this solution as a case analogous to that of the solution of pure zinc in sulphuric acid—an action which becomes more rapid under the influence of an alternating current. Other complex ions which can either be formed or destroyed under the influence of a continuous current are also formed by means of an alternating current—as in the case of copper, nickel, and cobalt dissolving in ammoniacal salts (carbonate, sulphate, or chloride). However, as the spontaneous action is zero, the reaction is less active than in the case of the cyanide, and the yields proportionately less.

γ -Chloroacetylacetic Ether.—M. Lespiau. —The author prepares γ -chloroacetylacetic ether, $\text{CH}_3\text{Cl.CO.CH}_2\text{CO}_2\text{C}_2\text{H}_5$. He finds it to be a colourless liquid of density 1.23, boiling at 105° at pressure 11 m.m. It distils at about 205° under atmospheric pressure, but considerable decomposition then takes place. Its colours dilute solutions of iron persalts a dark reddish violet. Its copper salt, $(\text{CH}_3\text{Cl.CO.CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2\text{Cu}$, crystallised from benzene, is anhydrous, of bright green colour, and decomposable about 160° .

Dichloromethene-dioxypyrrolylbenzene and Propylpyrocatechin Carbonate.—R. Delange. —Dichloromethene-dioxypyrrolylbenzene is an extremely active body which reacts immediately on water, alcohols, phenols, acids, acid anhydrides, ammonia, amines, &c. When carbon oxychloride acts on disodium propylpyrocatechin, the diphenolic carbonate is directly formed—a reaction which absolutely establishes the composition of the latter to be $\text{C}_3\text{H}_7\text{—C}_6\text{H}_4\text{—O—C(=O)—CO}$.

Glyoxylic Ureides. Allantoin and Allantoic Acid.—L. J. Simon. —Allantoin is soluble in aqueous potash. On immediate acidification it is reprecipitated without loss or alteration. If, however, the potash solution is left for some days, the solution contains a new potassium salt. Mulder isolated this, analysed it, and called it potassium allantate. Ponomareff isolated allantoic acid itself by utilising dilute sulphuric acid for the neutralisation. Finally, Grimaux effected the synthesis of allantoin by the action of glyoxylic acid on urea at 100° , without being able to isolate allantoic acid, which he considered as an intermediary in this synthesis. The author now repeats all these experiments, and prepares glyoxylic ureids—allantoin and allantoic acid.

Composition of Potato Starch. A. Fernbach. —Already noticed.

MISCELLANEOUS.

Royal Institution.—The following are the lecture arrangements at the Royal Institution, after Easter:—Prof. L. C. Miall, three lectures on "The Transformation of Animals"; Mr. L. Fletcher, three lectures on "Meteorites"; Mr. H. F. Newall, two lectures on the "Solar Corona"; Prof. Dewar, three lectures on "Dissociation"; Mr. H. G. Wells, two lectures on "Literature and the State"; Mr. Cyril Davenport, three lectures on (1) "Mezzotints," (2) "Cameos," (3) "Jewellery"; Mr. Donald Francis Tovey, three lectures on the "Sonata" (with musical illustrations); and Sir W. Martin Conway, two lectures on "Spitzbergen in the Seventeenth Century." The Friday Evening Meetings will be resumed on April 15, when Monsignor the Count de Vaya and Luskd will deliver a discourse on "Korea and the Koreans." Succeding discourses will probably be given by Lieut.-Col. David Bruce, the Dean of Westminster, Dr. P. Chalmers Mitchell, Mr. M. H. Spielmann, Prof. E. Rutherford, H.S.H. the Prince of Monaco, Prof. S. Arrhenius, and other gentlemen.

Aqueous Solutions of Colloidal Selenium.—A. Gutbier. —Solutions of colloidal selenium, obtained for the first time by Schulze (*Zeits. Prakt. Chem.*, 121, vol. xxxii, p. 390), are obtained by treating solutions of selenious acid with hydrate of hydrazine (1 part in 2000), hydrochlorate of hydroxylamine, or hypophosphorous acid. The solutions are red by transmitted light and a fluorescent blue by reflected light. They can be concentrated and filtered without changing; when submitted to electrolysis they deposit red selenium. By prolonged concentration of the solutions *in vacuo* over sulphuric acid, soluble colloidal selenium (hydrosol) is deposited, but more often the major portion is transformed into the insoluble colloidal selenium (hydrogel).—*Zeit. Anorg. Chem.*, vol. xxxii, p. 106.

Aqueous Solution of Colloidal Gold.—A. Gutbier. —For the preparation of such a solution, we dissolve 1 gm. of AuCl_3 in 1 litre of distilled water, and add carbonate of soda until neutral. The solution is then treated in the cold, and slowly, with a few drops of a very dilute solution of hydrate of hydrazine (the commercial solution at 50 per cent diluted with 2000 volumes of water). An excess of the hydrazine solution must be avoided. The colloidal solution is deep blue in colour both by reflected and by transmitted light. Its colour is similar to that of indigo. If by reflected light the liquor has a golden appearance it is because too much hydrazine has been added, and in such a case the precipitation of the gold takes place at once. The solutions are easily dialysed, and are very stable. Electrolysis causes the precipitation of the metal. —*Zeit. Anorg. Chem.*, vol. xxxii, p. 118.

Gravimetric Estimation of Tellurium by means of Hypophosphorous Acid.—A. Gutbier. —Even with very dilute solutions of telluric acid, hypophosphorous acid gives a brownish blue colouration, and thus enables us to detect tellurium qualitatively in solutions which do not contain the heavy metals, and which are free from free sulphuric or nitric acids; on the other hand, the presence of hydrochloric acid facilitates the reaction. For the quantitative estimation of the tellurium, the solution is treated with its own volume of hypophosphorous acid (a 50 per cent solution). Heat until the liquid, which is at first brown or blue in colour, becomes completely limpid. The precipitated tellurium is dried at 105° until the weight is constant. Instead of 55.57 and 79.95 of tellurium, the author obtained figures comprised between 55.20 — 55.82 and 79.84 — 80.05 . —*Zeit. Anorg. Chem.*, vol. xxxii, p. 295.

Iodimetric Estimation of Bismuth in the Form of Chromate.—E. Rupp and O. Schaumann. —The method described by Mohr in his *Treatise on Analysis* (seventh edition, p. 241, 1896) for the volumetric estimation of

bismuth does not give satisfactory results. This method, which consists of precipitating the bismuth by means of $\text{Cr}_2\text{O}_3\text{K}_2$, collecting the chromate of bismuth and titrating it with ammoniacal sulphate of iron, can be made perfectly exact by operating as follows.—The solution of bismuth containing the smallest possible quantity of free acid is poured into a known volume of a titrated solution of CrO_4K_2 (at about 5 per cent). The solution is then diluted, shaken energetically, and after ten minutes it is filtered. After making certain that the whole of the bismuth is precipitated, the excess of CrO_3 is estimated on a portion of the filtrate, by means of $\text{KI} + \text{SO}_4\text{H}_2$; the iodine set free is then titrated by means of $\text{S}_2\text{O}_3\text{Na}_2$.—*Zeit. Anorg. Chem.*, vol. xxxii., p. 359.

MEETINGS FOR THE WEEK.

- MONDAY, 21st.—Society of Arts, 8. (Cantor Lectures). "Recent Advances in Electro-chemistry," by Bertram Blount, F.I.C.
- TUESDAY, 22nd.—Royal Institution, 5. "The Doctrine of Heaven and Hell in Ancient Egypt, and the Books of the Underworld," by E. A. Wallis Budge, M.A., &c. Society of Arts, 4.30. "Cotton Growing in the British Empire," by Alfred Emmott, M.P.
- WEDNESDAY, 23rd.—Society of Arts, 8. "The Rural Housing Question," by T. Brice Phillips.
- THURSDAY, 24th.—Royal Institution, 5. "Shakespeare as Contemporaries knew him," by Sidney Lee, Litt.D.
- FRIDAY, 25th.—Royal Institution, 9. "Liquid Hydrogen Calorimetry," by Prof. Dewar, F.R.S.
- Physical, 5. "Note on the Measurement of Small Inductances and Capacities and on a Standard of Small Inductance" and "A Hot-wire Ammeter for Measuring very small Alternating Currents," by Prof. J. A. Fleming, F.R.S. "The Energy of Secondary Röntgen Radiation," by C. G. Barkla.
- SATURDAY, 26th.—Royal Institution, 3. "The Life and Work of Stokes," by Right Hon. Lord Rayleigh, F.R.S.

E. GEORGE & SONS,

BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.,

ARE OPEN TO PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1858 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.



OLD PLATINUM

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and Purchased.

MICA

Telephone No. 2248 Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., & London, 102 & 103, Minories, E.C.

Manufacturers of Mica Goods, or Electrical and ALL purposes. Contractors to His Majesty's Government.

ABSOLUTE ALCOHOL,

FREE FROM DUTY,

FOR SCIENTIFIC AND RESEARCH WORK IN LABORATORIES

To be obtained from

HUGO LORENZ,

7-8, Idol Lane, Great Tower St., London, E.C.

Licensed Trader in Alcohol and Spirits of Wine.

Stock kept in suitable packages ready for immediate use

MACMILLAN'S BOOKS ON CHEMISTRY.

SECOND EDITION, REVISED AND ENLARGED.

A SYSTEMATIC SURVEY OF THE ORGANIC COLOURING MATTERS.

Founded on the German of Drs. G. SCHULTZ and P. JULIUS. Revised throughout and greatly Enlarged by ARTHUR G. GREEN, F.I.C., F.C.S., Professor of Tintorial Chemistry at the Yorkshire College, Leeds; late Examiner in Coal-tar Products to the City and Guilds of London Institute.

Imperial 8vo, 21s. net.

JOURNAL of the SOCIETY of DYERS and COLOURISTS.—"The standard work of its kind in English."

Fractional Distillation.

By SYDNEY YOUNG, D.Sc., F.R.S., Professor of Chemistry in University College, Bristol. With 72 Illustrations.

Crown 8vo, 8s. 6d.

CHEMICAL TRADE JOURNAL.—Supplies a long-felt want. The whole of the chapters are easy and pleasant reading, and tempt the reader onward to the conclusion. We feel sure that every chemist who is interested in, or engaged with, any manufacturing process in which distillation is practised, will feel genuine pleasure in perusing this work, in studying the points of the various chapters, and in repeating some of the many experiments so fully described by the author."

THE CHEMISTRY OF PLANT AND ANIMAL LIFE.

By HARRY SNYDER, B.S.,

Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Agricultural Experiment Station.

Globe 8vo, 6s. net.

FIELD.—"As a handbook for use in schools of horticulture or in agricultural colleges, this handy volume is worth the attention of those interested in the science of chemistry as connected with the well doing of both plants and animals."

ELEMENTS OF INORGANIC CHEMISTRY.

By HARRY C. JONES,

Associate Professor of Physical Chemistry in the Johns Hopkins University.

Crown 8vo, 6s. 6d.

ROYAL COLLEGE OF SCIENCE MAGAZINE.—"We can without hesitation recommend this book to elementary students."

THEORETICAL ORGANIC CHEMISTRY.

By JULIUS B. COHEN, Ph.D., Lecturer on Organic Chemistry, The Yorkshire College; Lecturer in the Victoria University.

Globe 8vo, 6s.

NATURE.—"The book is well printed, and the proofs have evidently been very carefully corrected. Taken as a whole, we consider Dr. Cohen's book a very useful compilation."

A COLLEGE TEXT-BOOK OF CHEMISTRY.

By IRA REMSEN, President of Johns Hopkins University.

Extra Crown 8vo, 8s. 6d. net.

GUARDIAN.—"The author's skill in writing elementary textbooks is well known, and this work displays the features by which his other writings of the kind are characterised."

THIRD EDITION NOW READY.

INTRODUCTION TO PHYSICAL CHEMISTRY.

By JAMES WALKER, D.Sc., Ph.D., F.R.S.,

Professor of Chemistry in University College, Dundee.

Third Edition. 8vo, 10s. net.

CHEMICAL TRADE JOURNAL.—"A work we can earnestly advise the advanced chemist to study."

THE PRINCIPLES OF INORGANIC CHEMISTRY.

By WILHELM OSTWALD.

Translated with the Author's sanction by ALEXANDER FINDLAY, M.A., B.Sc., Ph.D. With 122 Figures in the Text.

8vo, 18s. net.

NATURE.—"Prof. Ostwald's style is excellent, and full justice is done to it by Dr. Findlay's translation; hence the book is most readable and interesting. It is unnecessary to mention that the work is entirely up to date."

MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

Vol. LXXXIX., No. 2313.

NOTE ON THE FORMATION OF SOLIDS AT LOW TEMPERATURES, PARTICULARLY WITH REGARD TO SOLID HYDROGEN.*

By MORRIS W. TRAVERS, D.Sc.,
Professor of Chemistry, University College, Bristol.

In the year 1902 Dr. J. J. van der Waals and I carried out some experiments on liquid and solid hydrogen with a view to determining its vapour pressure on the scales of the constant-volume helium and hydrogen thermometers. We found that hydrogen remained liquid down to 14.2° (He scale), the lowest temperature to which we could reduce a large mass of the liquid by means of the pump at our disposal. When, however, a small quantity of liquid hydrogen, cooled to 14.2° in a glass tube immersed in the liquid contained in the large vacuum vessel, was allowed to evaporate under reduced pressure, it solidified when the pressure fell to 49 or 50 m.m. of mercury. This pressure corresponds to a temperature of 14.1° on the helium scale. The presence of the solid was determined by mechanical means, and it was not possible to observe its appearance (*Phil. Trans.*, A, vol. cc., p. 170).

Dewar gives the melting-point of hydrogen at about 15° absolute, and the melting-pressure at 55 m.m. of mercury. He describes its appearance as that of "frozen foam," or as "clear transparent ice" (British Association, Presidential Address, 1902; see also paper on "Solid Hydrogen," *Brit. Assoc. Report*, 1899, reprinted in *Nature*; also *Roy. Inst. Proc.*, 1900).

It appeared to me worth while to carry out a few experiments to try to determine whether solid hydrogen formed definite crystal, or indeed whether the glassy substance was a true solid or merely a highly viscous fluid. My meaning will become clearer if I give an instance in which both such changes occur.

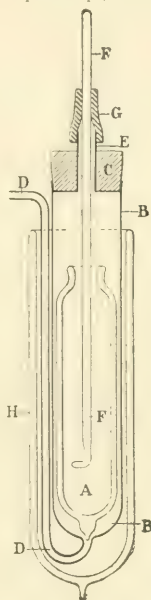
If an organic liquid, such as ethyl aceto-acetate, is cooled slowly to the temperature of liquid air it is converted into crystalline solid, the formation of the crystals commencing when the liquid is cooled to about -150° C., usually at several points on the side of the vessel, and spreading rapidly throughout the mass. If, on the other hand, the liquid is cooled very rapidly, a hard glassy substance is formed, and though crystals may begin to appear, they will only do so locally, as the velocity of crystallisation decreases rapidly as the viscosity of the liquid increases. The glassy substance is really a liquid of high viscosity; it is formed with perfect continuity from the normal liquid state, and should differ from the solid (crystalline) form in its physical properties. Such a substance might, for convenience, be called a pseudo-solid.

In investigating solid hydrogen the apparatus shown in the accompanying figure was employed. The liquid hydrogen was introduced into a small clear glass vacuum-vessel 15 c.m. long and 4 c.m. in internal diameter. This vessel was placed inside a glass tube, B B, which communicated with an exhaust pump through a tube, D D, sealed to it, and was closed by a rubber stopper, C. A short glass tube, E, 6 m.m. in diameter, passed through the stopper, and through it passed the stirring rod, F F. To allow of free rotating motion to the stirrer, and to make the apparatus gas-tight, a short piece of rubber tube, G, was passed over the end of the tube, E, and was wired to F. The lower part of the apparatus was contained within the vacuum vessel, H, which contained a small quantity of liquid air.

When the liquid hydrogen was made to boil *in vacuo*, its temperature fell, but the liquid did not appear to become more viscous. At length films of a colourless glassy sub-

stance formed at the surface, and broke away as the bubbles rose. After a short time the vessel became filled with these flakes, and while in this condition stirring, by giving the top of the rod F a rotatory motion, did not appear to indicate that the portion which remained liquid had undergone any considerable increase in viscosity. After a time the mass contained so much solid that it became pasty, and finally the whole of it appeared fairly homogeneous.

The solid evaporated fairly rapidly, so that after about ten minutes only a hollow cylinder of it, about 3 c.m. long and 2.5 c.m. in diameter, remained. This had the appearance of a film of ice which had partly thawed, consisting of clear granules connected by thinner and less transparent portions of solid. No crystals were observed on either of the three occasions on which the experiments were carried out. An attempt was made to examine the solid in the field of a polariscope, but it was unsuccessful.



Though there is no direct evidence of the formation of crystalline hydrogen, my experiments led me to the belief that solid hydrogen is a crystalline substance and not a pseudo-solid. The sharpness with which the solid hydrogen is formed, and the constancy of the apparent melting pressure, are distinct evidence in favour of this conclusion, though it must be allowed that the rate of change in viscosity, when the temperatures are measured on the Centigrade scale, will probably appear to be more rapid at low temperatures than at high temperatures.

The whole question of the formation of solids at very low temperatures is of great interest both from a physical and from a biological standpoint. It is quite possible that if living organisms were cooled only to temperatures at which physical changes such as crystallisation take place with measurable velocity, the process would be fatal, whereas if they once were cooled to the temperature of liquid air, no such change could take place within finite time, and the organism would survive. (Experimental results are given by Macfadyen, *Proc. Roy. Soc.*, 1900, vol.

* A Paper read before the Royal Society, February 1904.

lxvi., pp. 180, 339, 488; Swithinbank, *Proc. Roy. Soc.*, 1901, vol. lxviii., p. 502).

These experiments were made in connection with some investigations which were being carried out at University College, London, with the assistance of a grant from the Royal Society. As I am at the moment unable to continue the work, I have decided to publish this note.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 29TH, 1904.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, March 10th, 1904.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 203 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 203 samples examined by us during the month, all were clear, bright, and well filtered.

There has been a further excess of rain at Oxford during the past month; the actual rainfall measured was 2.98 inches. The average fall for February is 1.80 inches; thus we have an excess of 1.18 inches, which, if added to the previous excess for January, makes a total excess of 2.20 inches, or 56.7 per cent above the thirty-five years' average.

Our bacteriological examinations of 358 samples taken during last month have given the results recorded in the following table. Besides these samples we have examined 399 others from special wells, standpipes, &c., making 757 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	848
New River, filtered (mean of 68 samples) ..	33
Thames, unfiltered (mean of 25 samples) ..	19530
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 192 samples) ..	39
Ditto ditto highest	434
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	347
River Lea, from the East London Water Com- pany's clear-water wells (mean of 25 samples) ..	27

Of the 285 daily samples taken from the general filter wells of the Metropolitan Water Companies, seven samples, or 2.4 per cent, were sterile. Twenty-seven samples, or 9.4 per cent, contained more than 100 microbes, and of these, ten samples contained more than 150 microbes per c.c. The twenty-seven excess samples contained an average of 162 microbes per c.c. In January ten excess samples contained an average of 119 microbes per c.c.

The considerable increase in the number of microbes in the filtered water during the past month has been caused undoubtedly by the excessive rainfall and the flooded con-

dition of the Thames Valley. In January the unfiltered Thames water contained an average of 8797 microbes; in February this figure has risen to 19,530, while the numbers in the filtered samples have increased from 21 to 39. Considering the unfavourable condition of the Thames and Lea, the distribution of a filtered water containing no more than an average of 40 microbes per c.c. may be considered, under present circumstances, satisfactory.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

THE PRECIPITATION OF MAGNESIUM OXALATE WITH CALCIUM OXALATE.

By NICHOLAS KNIGHT.

THE purpose of this work was to determine the amount of magnesium oxalate that will precipitate with calcium oxalate in connection with the analysis of dolomite rock by different students. These rocks abound in Iowa and in many other portions of the United States. The specimens examined were variable mixtures of calcium and magnesium carbonates with silica, ferric oxide, and aluminum oxide. All were from the Niagara formation. Some proved to be nearly typical dolomites, which contain 45.65 per cent of magnesium carbonate and 54.35 per cent calcium carbonate.

At first a complete analysis of each specimen was made. The general method was to weigh about a grm. of the fine powder in a small beaker; to dissolve carefully (the beaker covered with a watch-glass) in pure dilute hydrochloric acid by gently heating to the boiling-point. The insoluble residue, consisting of silica, was filtered and determined. The amount of silica in these rocks is usually small, and this method, when compared with others, was found to give accurate results. A grm. or two of pure ammonium chloride was added to the filtrate from the silica, and at the boiling temperature it was treated with a small excess of ammonia to precipitate the iron and alumina. The filtrate from these was heated to boiling and precipitated with a $N/2$ solution of ammonium oxalate, care being taken to avoid much excess of the reagent. The precipitate was allowed to stand eight to twelve hours before filtering. The well-washed precipitate of calcium oxalate, with a small quantity of magnesium oxalate, was dissolved in warm dilute hydrochloric acid, and the solution was rendered alkaline with ammonia; this precipitates the calcium oxalate and leaves the magnesium in solution. This amount of magnesium and the main portion from the first calcium-magnesium precipitate were determined separately and weighed as magnesium pyrophosphate. The carbon dioxide was determined by the Bunsen method. After the complete analysis was made, only the small amount of magnesium, that which precipitates with the calcium, was determined.

1. Determinations by C. C. Carhart.

The specimen was nearly a typical dolomite, containing—

$CaCO_3$	53.78 per cent
$MgCO_3$	44.96 "
SiO_2	0.88 "
Fe_2O_3 and Al_2O_3 ..	0.38 "
	100.00 "

The small amount of MgO —i.e., the quantity precipitated with the calcium—was 0.08 per cent.

Eleven other determinations of this amount resulted as follows:—

1 0.26 per cent	7 0.13 per cent
2 0.16 "	8 0.11 "
3 0.20 "	9 0.17 "
4 0.29 "	10 0.20 "
5 0.31 "	11 0.14 "
6 0.11 "	

This is an average of 0.18 per cent MgO for the twelve determinations, corresponding to 0.378 per cent MgCO_3 .

The amounts obtained are small, and indicate that a sufficient quantity of ammonium chloride was added after removing the silica, and also that the ammonium oxalate was not added in large excess in the precipitation of the calcium.

II. Determinations by F. E. Welstead.

A complete analysis of the specimen gave—

CaCO_3	50.91 per cent
Larger quantity of MgCO_3	42.01 ..
Smaller quantity MgO, 0.70 per cent =	
MgCO_3	1.47 ..
SiO_2	2.08 ..
Fe_2O_3 and Al_2O_3	3.51 ..
	99.98 ..

2. MgO = 0.59 per cent
3. MgO = 0.47 ..
4. MgO = 0.75 .. } An average of 0.63 per cent.

III. Determinations by C. A. Utt.

1. The analysis of the specimen gave—

CaCO_3	52.92 per cent
MgCO_3	37.56 ..
MgO, 0.88 = MgCO_3	1.84 ..
Fe_2O_3 and Al_2O_3	6.26 ..
SiO_2	1.44 ..

- 100.02 ..
2. MgO = 0.96 per cent ..
3. MgO = 0.15 ..
4. MgO = 1.28 ..
5. MgO = 0.47 ..
6. MgO = 0.228 ..

In 1, 2, and 4 of this series, after dissolving the calcium and magnesium oxalates with hydrochloric acid and precipitating with ammonia, the calcium precipitate was at once filtered. It is therefore evident that the calcium was not all precipitated, and afterwards came down and was determined as magnesium. This easily explains the larger amounts obtained in these determinations.

Next such a mixture of pure Iceland spar and dolomite was taken that the calcium carbonate largely predominated.

1. The analysis of the mixture was—

CaCO_3	87.035 per cent
MgCO_3	10.828 ..
MgO = 0.47 = MgCO_3	0.990 ..
SiO_2	0.06 ..
Fe_2O_3 and Al_2O_3	1.08 ..

- 99.993 ..
2. MgO = 0.15 per cent.

Instead of a grm., but 0.2033 grm. of the original substance was used. The small quantity of MgO was 0.66 per cent. From the foregoing it appears that it makes no difference if the percentage of magnesium is relatively small or if a small amount of substance is used. About the same quantity of magnesium falls down with the calcium.

IV. Determinations by Miss L. D. Safely.

1. The analysis of the substance showed its composition as follows:—

CaCO_3	41.94 per cent
MgCO_3	42.15 ..
MgO = 0.81 = MgCO_3	1.70 ..
Fe_2O_3 and Al_2O_3	13.62 ..
SiO_2	0.88 ..

- 100.28 ..
2. MgO = 0.81 per cent
3. MgO = 0.78 ..
4. MgO = 0.80 ..
5. MgO = 0.72 ..
6. MgO = 1.20 ..

In the last case some calcium precipitated with the magnesium, because the calcium precipitate was not allowed to stand.

Next used a mixture of Iceland spar and dolomite in which the calcium carbonate largely predominated.

1. MgO = 0.47 per cent
2. MgO = 0.47 ..
3. MgO = 0.47 ..
4. MgO = 0.54 ..

Instead of a grm., used 0.3518 grm. of the original dolomite:—

MgO = 0.25 per cent.

Again, 0.2133 grm. gave—

MgO = 0.03 per cent.

Next a specimen of magnesite was used in which the amount of CaCO_3 was only 1.30 per cent. The small amount of MgO was 0.26 per cent.

The conclusion seems to be that the magnesium precipitated with the calcium varies from an almost inappreciable amount to a considerable quantity. It is therefore always better to dissolve the unwashed precipitates of calcium and magnesium in warm hydrochloric acid, then to add ammonia to precipitate the calcium. After standing a suitable time, the calcium may be filtered, and the filtrate can be added to the solution containing the main portion of the magnesium, or the two portions can be separately treated.

Chemical Laboratory, Cornell College,
January 1, 1903.

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.*

A STUDY OF PRASEODYMIUM: PREPARATION OF PURE MATERIAL—PRASEODYMIUM CITRATE.†

By CHAS. BASKERVILLE and J. W. TURRENTINE

We shall adopt, in reporting investigations upon the rare earths, the plan of succinctly stating in an introductory paragraph the facts observed and conclusions arrived at. Those desirous of familiarising themselves with the details may peruse what follows at leisure. Perhaps others may care to pursue a similar course. No doubt a wider dissemination of the actual results arrived at will come about, and the labours of abstractors be lessened and more accurate. Expediency influenced literary style before the Twentieth Century.

Synopsis.—This paper contains a description of a novel method for rapidly preparing pure compounds of praseodymium. It depends essentially upon saturating a concentrated water solution of citric acid with ammonium-free praseodymium hydroxide, in which the contaminating lanthanum is below 10 per cent. The solution is heated, whereby a new normal citrate is immediately precipitated and readily washed free from acid. The other procedures giving negative results were precipitations by potassium iodate, fractionating by hydrofluoric acid, gaseous hydrochloric acid, formaldehyde, fusion with potassium pyrosulphate, alkaline hydroxides, digestion in concentrated alkaline solutions, fusion with sodium peroxide, and attempts to form alums.

Fairly complete synopses of the observations leading to the breaking up of Mosander's didymium (*Lieb's Ann. Chem.*, xlv., 125) into several elements have been given in an historical consideration of the rarer earths (*Science*, 1902, N.S., xvii., 772; see also Dennis and Dales, *Journ. Am. Chem. Soc.*, 1902, xxiv., 425). To Dr. Carl Auer, without doubt, belongs the main credit of renewing interest in and stimulating the most modern assaults upon these interesting bodies. The former grew out of his patient research, resulting in the announcement of neo- and praseodymium (*Monatsh. Chem.*, 1885, vi., 477). The latter was

* This and the following dozen or more papers were presented in abstracts in a Lecture delivered before the New York Section under the title "The Rare Earth Crusade: What it Portends, Scientifically and Technically" (CHEMICAL NEWS, January, 1903).

† Presented at the Pittsburgh Meeting of the American Chemical Society, 1902. From the *Journal of the American Chemical Society*, 1904, xxvi., No. 1.

the outcome of his development and the extensive use of mantles composed of thorium and its co-geners for artificial illumination. The intimate relationship and the reciprocal dependence of pure and applied chemistry could not find a better illustration. The commercial demand for thorium compounds especially has caused extensive mining of and geologic investigations for the better known natural compounds, as cerite and monazite, and utilisation of several others previously regarded as rare curiosities of the mineral cabinet. In the extraction of the useful thorium oxide, there have accumulated tons of crude salt mixtures of the rarer elements biding a time of commercial extraction and utilisation.

The Welsbach Lighting Company, of Gloucester City, N. J., through their late chemist, the lamented Dr. Waldron Shapleigh, and his long time associate and successor, Dr. H. S. Miner, has aided scientific men frequently in generously loaning preparations extracted and often purified to a high degree. This, and a number of other researches which follow in this series, have been facilitated and rendered possible in certain cases by Mr. Miner's gratuities, and we wish here to express profound thanks.

During the preparation of pure thorium compounds, it was noted (by B., *Journ. Am. Chem. Soc.*, xxiii., 761) that a concentrated solution of citric acid, saturated with thorium hydroxide, precipitated a pure thorium citrate on heating. (By "pure thorium" is meant the "old thorium" without considering the recent researches of Schmidt, the Curies, Crookes, Rutherford, Brauner, Baskerville, and others). After destruction of the carbonaceous material and re-solution of the thorium oxide, no absorption bands were observable with a strong beam of light passing through 15 c.m. of the concentrated sulphate or chloride. In the preparation of thorium tetrachloride to be used in re-determining the atomic mass of thorium, a slight red in several cases and a green deposit in others (sometimes together) was formed in the hard glass tube several centimetres beyond the boat in which the mixture of carbon and oxide was heated. While the absorption spectrum has proved a most valuable means of investigating certain of the rarer earths, as has been well pointed out, it is not as extremely delicate as one might wish. Boudouard (*Comptes Rendus*, cxxvi., 12) has been able to separate small amounts of neodymium from quite pure yttrium preparations by repeated fractionations when the material had long since failed to show the absorption bands of the former complex. Cleve has observed the same with rather pure samarium (*CHEMICAL NEWS*, li., 145). It has been learned in this laboratory that when quite pure neodymium and praseodymium oxides are mixed with carbon and heated to a dull red in an atmosphere of chlorine they do not give rise to volatile bodies. However, we have learned that praseodymium chloride, when subjected to a temperature sufficiently high to soften combustion tubing, evolved a greenish body. (This will be taken up in one of the subsequent papers). Matignon has also observed the same in regard to neodymium, when a pink-coloured deposit is formed in the cooler parts of the tube (*CHEMICAL NEWS*, lxxxiv., 97; lxxxv., 132; *Comptes Rendus*, cxxiii., 5). From the colour of these bodies, it was immediately assumed that, in spite of the prolonged and painstaking method of preparation, our pure thorium compounds (*loc. cit.*) still retained a trace of the constituents of didymium, which hangs on in other cases. Investigations were at once begun therefore to learn the conduct of these elements with citric acid—the only novel feature in the method of purification not previously tested.

Before giving the result of those experiments, it may be well to state that up to that time the chlorine used had been generated by the action of pure concentrated hydrochloric acid upon re-crystallised and granulated potassium dichromate. Subsequently a cylinder of pure chlorine was substituted, with a complete cessation of the trouble. These red and green deposits were very small, but persisted in forming as long as the chlorine was prepared by the chromate method, and finally proved to be due to chromium.

This was an observation of no little interest, as the chlorine gas was thoroughly scrubbed by passing through four wash-bottles of concentrated pure sulphuric acid (98 per cent) and two columns of beads and one tower of pumice saturated with the same desiccating agent before entering the combustion tubing. One is immediately reminded of Crookes's difficulty in preventing a back flow of mercury vapour in evacuating the bulbs for his beautiful phosphorescence spectra examinations, when he states there is "no use trusting to a solid reagent to absorb a gaseous body" (*CHEMICAL NEWS*, liv., 29).

Praseodymium ammonium nitrate prepared by the method of Auer (*Monatsh. Chem.*, vi., 477) was converted into the hydroxide, and washed by decantation until the ammonium salts were virtually removed. Twenty-five c.c. of a concentrated water solution of citric acid were saturated with the praseodymium hydroxide by shaking in a glass-stoppered bottle; the undissolved hydroxide filtered away, and the green solution heated. Immediately a pale green amorphous precipitate formed, settled upon the bottom of the vessel, was easily filtered, and washed with hot water.

Similar experiments were carried out with neodymium and lanthanum hydroxides. The former is about one-tenth as soluble in citric acid as praseodymium hydroxide, and is not precipitated on boiling, until the solution is very concentrated.

Lanthanum hydroxide is intermediate in its solubility and not precipitated at once on boiling. It requires concentration and continued heat, although both of these substances allow tough, whitish precipitates to form, when a very strong solution is permitted to stand some days at the temperature of the room. Perhaps here we may have to do with such colloidal compounds of the rare metals as mentioned by Delafontaine (*CHEMICAL NEWS*, lxxiii., 284). This point requires investigation, however.

Numerous attempts were made to apply the observations noted to separating lanthanum from the didymiums as they occur in monazite sand and other rare earth minerals, but with little success. The lanthanum apparently causes a supersaturated solution to form, which it is difficult to precipitate by heat; further, when a precipitate forms, it contains all three of the elements* in all the fractions obtained.

The praseodymium ammonium nitrate contained about 10 per cent of lanthanum. One precipitation, according to the procedure mentioned, was sufficient to give a body absolutely free from lanthanum, as shown by the arc spectrograph made with a concave Rowland's grating, 15,000 lines to the inch and 21 feet diameter.† This was determined frequently with that part of the spectrum which shows the strong lanthanum lines.

Praseodymium Citrate.—The body was prepared on different scales, using from a few grams. of praseodymium ammonium nitrate to as much as 4 kilograms., in one place. The cold citrate solution (as much as 5 litres of the solution being used in certain experiments) was placed in a tall cylindrical precipitating jar, and stirred by a water motor while the hydroxide was added to complete saturation, the agitation being continued from two to four hours. The temperature was kept down by placing the jar in running water. The turbid liquid was then quickly filtered by upward suction through an unglaazed porcelain pear-shaped bomb. The beautiful, clear, leek-green solution was heated in large Jena glass beakers submerged in baths of boiling water, and filtered through a hot funnel, suction being applied at times, by means of the biscuit-ware mentioned, a most useful piece of apparatus when working on the large scale in the laboratory. The precipitate was readily and quickly washed by boiling water, in which it is insoluble (the washings being kept separate), until the filtrate was no longer acid to litmus.

* The term "element" is used advisedly here, although there is no doubt of neodymium and praseodymium being "complexes," as will be shown in later papers. At present, however, most chemists look upon these bodies as simple.

† Dr. W. J. Humphreys, of the Rouss Physical Laboratory, University of Virginia, kindly prepared these plates, a discussion of which he will publish in due time.

The precipitate, when dried, was a loose powder, amorphous, of a beautiful pale green colour. On analysis the following results were obtained:—

Found.	Calculated for (Pr=140.5)	
	Pr(C ₆ H ₅ O ₇) ₃	Pr(C ₆ H ₅ O ₇) ₃ ·H ₂ O
Oxide (black) 48.83 48.70	As PrO ₂ .. 52.35	49.64
	or As Pr ₄ O ₇ .. 49.90	48.49
Carbon .. — —	21.05 21.18 21.85	20.72
Hydrogen .. — —	1.46 1.86 1.52	1.44

Remarks and Precautions.

Ammonia prevented the formation of this normal citrate in this manner; hence the necessity for thoroughly washing the hydroxide. The citrate is soluble in ammonium citrate. So far, we have not sought to separate the double salt which is evidently formed.

As is well known, lanthanum hydroxide, and in fact most of these so-called trivalent rare earth hydroxides, combine with the carbon dioxide of the air, whereby a partial solution results, and an increasing turbidity of the wash-water that is decanted is observed, depending upon the poverty of ammonia and its salts. We avoided this by rapid working, making use of the largest unglazed porcelain suction filter made.

The filtrate from the citrate precipitate was concentrated by heat, and successive precipitates formed, and were separated. They were mealy precipitates, which, on drying formed light but tough masses, each succeeding mass being tougher than the preceding and more difficult to disintegrate into a powder. The fifth appeared in the solution as flocculent agglomerations like paper pulp, and, on drying, became hard and leathery. The following precipitates presented the same appearance, and were almost white in colour. The change in form and the disappearance of the green colour were progressive throughout each series that was carried out. The percentage of oxide in the bodies correspondingly decreased from 48.83 per cent to 35.77. The third precipitate gave strong lanthanum lines in the arc spectrum. They were not further investigated, and are hardly worthy of the time necessary in view of the following facts:—

In attempting to purify praseodymium on the large scale by this method, we observed that when the percentage of lanthanum rose above twenty, no success attended our efforts. By the method of Auer (*loc. cit.*) a large proportion of the lanthanum is first crystallised out as double ammonium nitrate. It has been observed by Dennis (*Journ. Am. Chem. Soc.*, 1897, xix., 800), Bettendorf (*Liebigs Ann. Chem.*, cclvi., 163), and others, that didymium breaks up the more readily, accompanied with less frequent formation of supersaturated solutions, difficult to handle, when lanthanum is present in notable amounts. By this modified Welsbach method, praseodymium may be readily separated from neodymium, but it is a more difficult proposition to secure the latter devoid of the former. To separate pure neodymium, Boudouard (*Comptes Rendus*, cxvii., 12; *CHEMICAL NEWS*, lxxvii., 193) and Muthmann (*Ber. d. Chem. Ges.*, xxxi., 1731) advocate crystallising the double potassium sulphate, but this does not leave either one free from lanthanum, unless the material is subjected to a prolonged series of fractional crystallisation, almost exasperating in their consumption of time, as all who have worked with these rare earths know.* With these facts in mind, it becomes evident at once that a quick method for the separation of 5 to 10 per cent of lanthanum is worth while, and one that separated the praseodymium absolutely pure is most desirable. In fact, one phase most engrossing rare earth work at present has to do with finding such means for the separation of pure compounds.

Our last work was with 7 kilograms. of praseodymium ammonium nitrate free from neodymium, but containing more than 20 per cent of lanthanum. The material had undergone 300 crystallisations and came from about 100 tons of monazite. A water solution was precipitated by

ammonium hydroxide in large glazed earthenware vessels (100-litre capacity), provided with spiral outlets by which, on removing rubber stoppers, the supernatant liquid might be drawn from different heights. The excess of ammonium nitrate was thus removed by two washings to prevent the attack of platinum (by its decomposition) in which the entire precipitate was ignited in portions. To decrease the percentage of lanthanum present, the method of Auer (*Monatsh. Chem.*, v., 508) proved satisfactory, and is not expensive, viz., the mixed oxide were added to dilute nitric acid until almost saturated, an account being kept of the weight, and then as much more oxide added. The more basic lanthanum forms the nitrate and remains in solution, taking a part of the praseodymium, as might be expected, while the major portion of the latter oxide is undissolved. Lanthanum, of course, is still present in the undissolved portion, but in much smaller percentage. The difference in the affinity, at least towards nitric acid, is not sufficient to serve as a method for bringing about a rapid separation of these bodies in the pure state. The solution was separated by filtration, washed once or twice, and the respective fractions converted into hydroxides of the earths free from ammonia. Citric acid saturated with the hydroxide from the nitrate solution gave no precipitate on boiling, while that from the undissolved oxides immediately gave an excellent separation of the citrate, yielding over a kilogram. of pure praseodymium oxide on ignition. The material is absolutely free from lanthanum, and as pure as that used by Jones (*Am. Chem. Journ.*, 1898, xx., 5, 345) in his atomic weight determination. It may be well to state that Dr. Humphreys made the spectrographs for Dr. Jones and had the plates for comparison. Although chemically pure citric acid free from lead, ammonia free from silica and sulphuric acid, and nitric acid giving no residue on evaporation, and re-distilled water were used, the preparation contains such impurities as would be gathered from the containers used in the process, but they are in such small amounts as not to vitiate the results reported in several of the following papers, and of such a character that they may be readily removed at the stage it is deemed necessary.

This material as a neutral nitrate, examined at various dilutions and different thicknesses, showed an absorption spectrum that is given for the normal so called elementary praseodymium (bands 569, 482, 459, and 443), and was used in the other work reported in this series. The absorption spectrum was examined and photographed with a Steinheil grating (14,438 lines to the inch) spectroscopically, as described by Dennis (*Journ. Am. Chem. Soc.*, xciv., 415). The instrument is essentially the same, except that it is a size larger and has a quartz-slit. The source of light used at first was a 100-candle power Edison incandescent light with a helixoid filament. Latterly we have substituted a 600-candle power arc light enclosed in a projection lantern which serves to focus the rays upon the slit. The bright lines of carbon and its impurities, once noted, do not interfere with the observations of the bands. The instrument was purchased with a grant from the Bache Fund of the National Academy.

During the progress of this work, the application of other methods for accomplishing the same object were attempted. Separating by potassium iodate, hydrofluoric acid, crystallising a concentrated chloride solution by saturating with gaseous hydrochloric acid, formaldehyde, fusion with potassium pyrosulphate, alkaline hydroxides, digestion of rare earth* hydroxides in concentrated alkaline solutions, fusion with sodium peroxide, and endeavouring to form alums, were tried, and they either gave negative results or such as did not warrant pursuit.

Conclusion.—Pure praseodymium compounds may be prepared by heating a saturated citric acid solution from which praseodymium citrate separates when the percentage of lanthanum is below 10, in a few hours, while by the former methods weeks or even months were required.

* A paper follows, giving a new method for freeing neodymium of lanthanum.

* See papers on "Lanthanates," "Neodymates," "Double Sulphates," &c., following.

THE ELEMENTS: VERIFIED AND UNVERIFIED.

By CHARLES BASKERVILLE, Ph.D., F.C.S., Smith Professor of General Chemistry, University of North Carolina.
(Continued from p. 137).

LIST OF PROPOSED CHEMICAL ELEMENTS.

NOTE.—The italicised names are elements which have been tried and found wanting; those in small capitals have been verified beyond question as distinct, although in specific cases evidence is had that they are complex. All others uniformly stand before the bar of judgment. The arrangement is chronological. Due to pressure of affairs, it has been quite impossible in some cases to consult the original papers, hence part of the table is composed of second-hand and meagre information. Every source available has been drawn upon, as Venable's "The Elements, Historically Considered" (*Journ. Eliza. Mitchell Scientific Society*, 1887, iv., 36), which unfortunately gives no references; Winkler's "The Discovery of New Elements within the last Twenty-five Years" (Lecture before the German Chemical Society, *Smithsonian Report* for 1897, 237); Cleve's "Marignac Memorial Lecture," 1895; "Rise and Fall of the Delinquent Elements" (*CHEMICAL NEWS*, 1890, xlii., 208); "List of Elementary Substances announced from 1877 to 1887" (*CHEMICAL NEWS*, lvi., 188), by the lamented H. Carrington Bolton, to whom I cannot too strongly emphasise my indebtedness for his ever-ready help and sympathy. It is my desire to have this as complete and authentic as possible. I therefore beg that all information as to omissions and corrections be forwarded me (Chapel Hill, North Carolina, U.S.A.); it will be gratefully acknowledged.

Date.	Name.	Source.	Authority.	Reference.	Remarks.
1777 1778	<i>Terra nobilis</i> . MOLYBDENUM.	Diamonds. Lead ores.	Tobern Bergman. Scheele.	Kong. Vet. Akad. Handl., 247.	Molybdena meant number of substances carrying lead. Hjelm (1790) (<i>Ann. de Chim.</i> , 4, 17) isolated the element.
1780	<i>Hydroxidum</i> .	Cold-short iron.	Meyer.	Schiff. Ges. Nat. Freunde, Berlin, H., 334; III., 380.	Wassereisen, obtained by dissolving crude iron in acids.
1781	TUNGSTEN.	Scheelite.	Scheele.	Kong. Vet. Akad. Handl., 89.	Klaproth proved it to be iron phosphide. Acid separated from scheelite. Bros. D'Elhujar proved it to be in wolframite. The two minerals had long been known.
1781 1782 (1798)	<i>Siderum</i> . TELLURIUM.	Cold-short iron. Native.	Bergman. von Reichenstein and Klaproth.	Crell's Ann., 1798, 1, 91.	Proved to be iron phosphide. Regarded <i>aurum paradoxum</i> or <i>metallum problematicum</i> —and still is.
1784 1788	Saturnum. <i>Dianautispatherde</i> .	Lead ore. Corundum.	Monnet. Klaproth.	Journ. de Physique, 28. Beschalt Ges. Nat. Freunde, Berlin, 8, 4.	Composed of silicon, iron, and aluminum oxides.
1789	URANIUM.	Pitchblende.	Klaproth.	Crell's Ann., 2, 387.	Metal not separated until 1842, then by Peligot (<i>Ann. de Chim.</i> , 5, 5).
1789	ZIRCONIUM.	Zircon.	Klaproth.	Klaproth's Beitrage, 1, 203; Crell's Ann., 1, 7; <i>Ann. de Chim.</i> , 1, 238.	See work of Berlin (1860).
1799	<i>Australium</i> or Syd- neum.	Sand.	Wedgewood.		Hatchett showed this Australian sand to contain iron, aluminum, and silicon oxides.
1791	<i>Mnuchite</i> .	Magnetic Sand.	McGregor.	Crell's Ann., 1, 40, 103.	Klaproth four years later discovered titanium (Beitr., 1, 233), and in 1797 found it to be identical with menachite (Beitr., 2, 236).
1794	YTTRIUM.	Gadolinite.	Gadolin.	Sv. Vet. Akad. Handl., 1794, 137; <i>Crell's Ann.</i> , 1796, 1, 313.	Named by Ekeberg (1799) (<i>Crell's Ann.</i> , 2, 63).
1799 1800	<i>Nameless earth</i> . <i>Augusterde</i> .	Beryl.	Fernandez. Trommsdorff.	Scherer's Allg. S., 4, 312; Gehlen's Allg. J., 1, 445.	Vauquelin showed it to be calcium phosphate, now known as the mineral apatite.
1800	<i>Andronia</i> .	Charcoal and salt- petre.	Winterl.	Gehlen's J., and Gilbert's Annalen.	Committee of the French Academy showed it was composed of lime, alumina, silica, and iron oxide.
1800	<i>Tielike</i> .	Marble.	Winterl.		

1801 1803	<i>Alkali primum</i> , <i>Erythronium</i> .	Hahneman, del Rio.	Ann. der Phys. und Chem., 71, 7.	Proved to be borax. Because became red when heated with acids. Later Descottis and del Rio concluded it was impure chromium oxide (Ann. de Chim., 53, 268). See Vanadium.
1801 (1844)	Columbite.	Hatchett, (Rose).	Crell's Ann., 1802, 1, 107; 267, 452.	After Wollaston (1809) (Phil. Trans., 99, 246) had said columbium and tantalum were the same and it was accepted, effective work was done by H. Rose (Pogg. Ann., 70, 572; 71, 159, and many later), who re-named it niobium.
1802	Finnish tantalite and ytrotantalite.	Ekeberg.	Scheerer's J., 9, 547; Crell's Annalen, 1903, 1.	Important work on this element also done by Berzelius (Pogg. Ann., 4, 6) and H. Rose (Pogg. Ann., 15, 145, &c.). See Columbium.
1803 1804	Cerite and ochro-terde.	Proust, Berzelius and Heskinger.	Journ. de Physique, Gehlen's Ann., 4, 403; and 2, 397.	This complex later shown to contain lanthanum, but the name remains for the element.
1805 1811	Niocolanum, Jantanium.	Klaproth, Thomson.	Gilb. Ann., 10, 477; Phil. Mag., 36, 278; and Gilb. Ann., 44, 113.	Shown to be mixture of nickel, cobalt, arsenic, and iron. Identity with cerium proved by Wollaston.
1817	Gadolinite.	Berzelius.	Afhandl. i. Physik, Kemi Och Min., V., 70; and Ann. Chem. Phys., 5, 8. Gilb. Ann., 59 and 62.	Berzelius later (K. Vet. Acad. Handl., II., 4, 184) proved this to be yttrium phosphide.
1818	Yastrom or Strium.	Vest.	Gilb. Ann., 60 and 64.	Faraday showed it to be a mixture of nickel, iron, sulphur, and arsenic.
1818	Wollastium.	Lampadius.	Gilb. Ann., 65 and 66.	Strömyer showed it consisted of nickel, arsenic, &c.
1820	Crocolanium.	Trommsdorff.	Gilb. Ann., 65 and 66.	Wodniks, present mineral petersdorffite. Discoverer afterwards demonstrated it to be mainly calcium and magnesium salts with copper and iron impurities.
1820 1821 1828	<i>Primum</i> <i>affine</i> , <i>Thontite</i> .	Mills, Brugnatelli, Berzelius.	Gilb. Ann., 67; K. Sv. Vet. Akad. Handl., 1. Ann. d. Phys., 16, 685.	While no doubt a definite element as accepted, there is no question as to its complexity (see Chrouschoff, Schmidt, Curie, Rutherford, Biauener, and Baskerville).
1828	Platinumore (Urbis).	Osann.	Pogg. Ann., 14, 340.	Not to be confounded with the well-known ruthenium of Claus. Said to be metal of a golden lustre. Osann previously (Pogg. Ann., 13, 287) gave the name to reddish volatile prisms pronounced by Berzelius new (<i>trile</i> Howe's Vice President Address before this Section, 1900, 94).
1828	Platinumore (Urbis).	Osann.	Pogg. Ann., 14, 340.	Shown to be a mixture of oxides of titanium, zirconium, and silicon by Osann (1829) (Pogg. Ann., 15, 158).
1828 1830	Platinumore (Urbis), Swedish iron ore.	Osann, Sachsion.	Pogg. Ann., 14, 340; Am. Journ. Sci., 1, 90, 486.	Proved to be impure iridium by the discoverer. About same time Wobler showed identity of this with erythronium (Pogg. Ann., 24, 89).
1836 1836	Dontium, Iridium.	Richardson, Boase.	Ann. Chem. Phys., 19 and 23. Thomson's Records, Gen. Science, 4, 20.	Identical with glaucum, as shown by Heddle. Identical with donum.
1839	Urbis HANMUM.	Mosander.	Pogg. Ann., 16, 648; and 17, 207.	Much work done by Biauener looking towards its complexity; so far regards it simple.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 3rd, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

(Concluded from p. 142).

40. "Photochemically Active Chlorine." (A Preliminary Notice). By CHARLES HUTCHENS BURGESS and DAVID LEONARD CHAPMAN.

By taking advantage of several new facts, the authors have succeeded in showing that the activity of a mixture of hydrogen and chlorine depends entirely on the condition of the chlorine. Draper originally maintained that this was the case, but Bunsen and Roscoe were unable to repeat his experiments, and Mellor, accepting the results of Bunsen and Roscoe, has constructed his working hypothesis on the assumption that Draper is wrong. P. V. Bevan (*Phil. Trans.*, 1903, ccii., 71) has quite recently shown that similar mixtures of hydrogen with insolated and unisolated chlorine exposed to light under the same conditions behave somewhat differently, the period of induction of the former being slightly shorter. The work of Bevan shows that before hydrochloric acid can be formed, some change in the chlorine alone must take place, but it may also be necessary for a further change to occur which can only be effected in the presence of hydrogen, or, in terms of this author's hypothesis, it may first be necessary for complex molecules of chlorine and water to be formed, and then for the hydrogen to react with these, forming complexes containing water, chlorine, and hydrogen, both changes requiring a finite time for their completion.

That a saturated solution of chlorine in water can exist either in an active or in an inactive condition is shown in the following way:—A mixture of hydrogen and chlorine contained in a Bunsen and Roscoe's actinometer was exposed to light until the period of induction was passed. It was then vigorously shaken so as to mix the gas and liquid thoroughly. When the mixture was again exposed to light, a second period of induction was observed, which, however, was not so long as the first. A still shorter period of induction was indicated when the mixture had again been shaken, until after repeating the above process several times no difference could be noticed in the rate of combination before and after shaking, thus proving that the liquid in the bulb had become active. The change which precedes the formation of hydrogen chloride undoubtedly extends to the aqueous solution.

It was next shown that a mixture of hydrogen and chlorine which had passed through the period of induction could again be rendered inactive by shaking the mixed gases with either water, hydrochloric acid, hypochlorous acid, or chlorine water, and further that a mixture of hydrogen and chlorine which had been agitated with water showed a much longer period of induction than one which had not been thus treated.

An apparatus was devised into which chlorine could be passed and treated in any desired manner before being mixed with hydrogen. Into this apparatus, chlorine was passed and shaken with water. The chlorine water thus formed was removed, and the gas again shaken with a fresh supply of water, the operation being repeated several times. The chlorine which had been thus treated was then mixed with an equal volume of hydrogen and exposed to light, when the period of induction lasted for over an hour.

In the next experiment, the chlorine was constantly shaken with the liquid contained in the apparatus, and exposed to a strong light in order to render both the liquid and the gas active; the gas was then mixed with hydrogen in the dark and exposed to light. There was no period of induction; combination of hydrogen and chlorine took place immediately, and no variation in the rate of combination could be observed throughout the reaction.

These results indicate (1) that a solution of chlorine exists either in an active or in an inactive state; (2) that the period of induction is entirely due to the condition of the chlorine.

41. "The Union of Hydrogen and Chlorine. VIII. The Action of Temperature on the Period of Induction." By JOSEPH WILLIAM MELLOR.

Measurements of the duration of the period of induction at different temperatures from 3° up to 50° show (1) that the period is shorter the higher the temperature; (2) that above 38°, disturbing effects, probably due to the presence of water vapour, obscure the influence of the increased temperature.

42. The Union of Hydrogen and Chlorine. IX. Further Experiments on the Action of Light on Chlorine." By JOSEPH WILLIAM MELLOR.

Bevan has recently shown that the activity of chlorine after exposure to sunlight, first observed by Draper, is destroyed by bubbling the chlorine through water, as in Bunsen and Roscoe's experiment. Bevan supposes that the union with hydrogen still proceeds through the intervention of the intermediate compound, $\text{Cl}_2\text{yH}_2\text{O} \cdot \text{H}_2$, as suggested in the author's paper (*Trans.*, 1902, lxxxi., 1280). Two bulbs of ordinary moist chlorine were exposed to sunlight for ten minutes, and afterwards mixed with moist hydrogen. The duration of the period of induction with this mixture was compared with that of a similar mixture made in darkness. Two more bulbs of chlorine, dried with phosphoric oxide, were treated in exactly the same way. The periods of induction were relatively as follows, the expansion being corrected for the Budde effect:—

Standard.	Moist.	Dry.
I	0.5	1.0
I	0.3	0.9

The results show that the greater chemical activity of insolated chlorine is intimately associated with the presence of steam. The alternative hypothesis, put forward in the above-cited paper, is just as satisfactory as the intermediate compound theory.

43. "Additive Compounds of Unsaturated Cyclic Ketones with Hydrogen Cyanide." By ARCHIE CECIL OSBORNE HANN and ARTHUR LAPWORTH.

The applicability of the general method for bringing about the addition of hydrogen cyanide to the ethylenic union in α -unsaturated ketones, nitriles, &c., recently worked out by one of us (*Trans.*, 1903, lxxxi., 999), is being systematically investigated, particularly with regard to the open chain and cyclic ketones and aldehydes.

Carvone, in presence of potassium cyanide, unites with one molecular proportion of hydrogen cyanide in the cold. The product, which is formed in nearly quantitative amount, is a nitrile, $\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{CN}$, melting at 93.5–94.5°, which, on hydrolysis, yields two isomeric unsaturated acids, $\text{C}_{10}\text{H}_{13}\text{O} \cdot \text{CO}_2\text{H}$, melting at 137° and 96–97°. The foregoing nitrile gives a cyanohydrin, $\text{C} \sim \text{C}_{10}\text{H}_{15}(\text{OH}) \cdot \text{CN}$, melting at 106–108°, which is easily hydrolysed, forming the acids, $\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}$ and $\text{C}_{12}\text{H}_{16}\text{O}_4$, which are possibly mixtures of isomeric acids.

Pulegone behaves somewhat similarly; the first additive product is the nitrile, $\text{C}_{10}\text{H}_{17}\text{O} \cdot \text{CN}$, which melts at 160.5°.

A number of other derivatives of the foregoing compounds have been obtained, and will be described in due course.

44. "The Formation of Periodides in Organic Solvents." By HARRY MEDFORTH DAWSON.

The formation of potassium periodides in various organic solvents has been studied by determining the composition of such solutions when saturated either with potassium iodide or with iodine.

The aromatic nitro-compounds investigated, such as nitrobenzene, *o*-nitrotoluene, *m*-nitrotoluene, and *o*-nitroanisole, show a very similar behaviour, and under conditions favourable to the formation of the highest possible periodide, namely, saturation of the solution with regard to

iodine, the enneaiodide, KI_9 , is the essential component of the solutions. The composition of the solutions saturated with respect to potassium iodide indicates that increasing concentration favours the formation of periodides of gradually increasing complexity.

By a method devised for the study of solid aromatic nitro-compounds, it is shown that these exert an influence on the formation of soluble periodides which is in many respects similar to that of nitrobenzene.

Other solvents, including nitromethane, nitropentane, ethyl alcohol, propionitrile, ethyl acetate, ethyl bromide, and isobutyl alcohol, have also been investigated.

45. "The Action of Sodium Hypochlorite on the Aromatic Sulphonamides." By HENRY STANLEY RAPER, JOHN THOMAS THOMPSON, and JULIUS BEREND COHEN.

The authors have continued the investigation described in the preliminary notice published in the *Proceedings* (1901, xvii., 262), and have added the following facts:—

Benzenesulphon-o-toluidide (m. p. 123–124°), when dissolved in acetic acid and treated with sodium hypochlorite, yields the *chloroamide*, $C_7H_7NClSO_2 \cdot C_6H_5$, melting at 99–100°; this product, on heating with acetic acid, gives *benzenesulphon-5-chloro-o-toluidide* (m. p. 124–125°). *Benzenesulphon-m-toluidide* (m. p. 95°) gives a sodium compound, $(C_6H_5Cl)(CH_3) \cdot NNa \cdot SO_2 \cdot C_6H_5$, melting at 275–280°, which is decomposed by acetic acid, and yields *benzenesulphon-6-chloro-m-toluidide*. With an excess of hypochlorite, *benzenesulphon-2:6-dichloro-m-toluidide* (m. p. 114°) is formed. *Benzenesulphon-p-toluidide* forms *benzenesulphon-3-chloro-p-toluidide* (m. p. 110°).

Benzenesulphon-4-m-xylidide (m. p. 124–125°) gives *benzenesulphon-5-chloro-4-m-xylidide* (m. p. 148–149°) when heated with the hypochlorite solution at 50°.

Benzenesulphon-a-naphthalide (m. p. 168°) is quite unaffected by the hypochlorite even on warming. *Benzene sulphon-1-naphthalide* (m. p. 97–98°) forms a sodium compound, which, when decomposed with acid, gives *benzenesulphon-1-chloro-8-naphthalide* (m. p. 130–131°).

Chattaway and Orton have shown that by the action of sodium hypochlorite on the acyl derivatives of the aromatic amino-compounds, the halogen in the first instance enters the ring in the para-position with respect to the amino-group, and then selects the ortho-position. The orienting effect of the sulphonic group is different. The foregoing results show that in the first instance the halogen seeks the ortho-position with respect to the amino-group. If a methyl group is present and if the para-position to the amino-group is free, the conditions are modified, and the halogen enters either the ortho-position to the methyl radicle or the para-position to the amino-group. It is interesting to note that the action of the hypochlorite is retarded in the *o*-substituted sulphonamides; those of *o*-toluidide and xylidide react with difficulty, whilst that of *a*-naphthylamine, which may be regarded as an ortho-substituted compound, is quite unchanged.

PHYSICAL SOCIETY.

Ordinary Meeting, March 11th, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A PAPER ON "The Whirling and Transverse Vibrations of Shafts" was read by Dr. CHRRE.

The "whirling" of rotating shafts was treated theoretically by Prof. Greenhill in the *Proceedings of the Mechanical Engineers*, 1883, and by Prof. Dunkerley in *Phil Trans.*, Sect. A, 1894. The latter considered the subject in great detail. He made a number of calculations based on two methods—one the same as Prof. Greenhill's, the other due apparently to Prof. Osborne Reynolds—and he compared them with experiments made on a model shaft and pulleys. The second method was employed in all cases where the shaft was loaded; it is dependent on a hypothesis which, as presented by Dunkerley, is largely empirical. The present

paper proceeds from a different standpoint, based on the true nature of the relationship between whirling and transverse vibrations, which seems to have escaped previous notice. It shows how the mathematical results obtained by Prof. Dunkerley can be derived by a less cumbersome treatment, and how in many instances they admit of great simplification, without sensible loss of accuracy. It is also shown how loaded shafts can be dealt with, without recourse to Dunkerley's hypothesis; at the same time some light is thrown on the relation of this hypothesis to theory.

Six main cases are considered, in which the shaft is variously supported; in some of them numerical results are deduced for comparison with Dunkerley's experiments. Some data are given for the stresses due to "centrifugal forces" answering to the velocities at which whirling should appear, and attention is thus called to the necessity of taking these stresses into account when considering the question of safety.

In the main part of the paper results are quoted with only a general indication of the mathematical methods employed; but these methods are illustrated in a short appendix.

The CHAIRMAN said there was one point he would like to bring out in connection with Dr. Chree's paper. The author had referred to a theorem due to Lord Rayleigh: a theorem which he knew well in its application to sound, although he had never seen it employed in connection with rotating shafts. The theorem is that in any vibrating system the period of natural vibrations is a stationary period, so that the application of any small external force produces only a second-order change in the period. By use of this theorem it is possible to assume a definite law and calculate periods with sufficient accuracy by working with expressions much less complicated than would otherwise be the case.

A paper entitled "Notes on Non-homocentric Pencils, and the Shadows Produced by them. Part II. Shadows Produced by Axially Symmetrical Pencils possessing Spherical Aberration," was read by Mr. W. BENNETT.

This paper deals with the shadows obtained by interposing a straight wire near the focus of a pencil proceeding from a lens or mirror uncorrected for spherical aberration. A method is described for drawing sections of the wave-front in the neighbourhood of the focus. A simple physical explanation of the shadows is given by means of the wave-fronts; it is shown that the real shadow consists in general of two branches, one closed and the other open, with a ϕ -form as a symmetrical special case. The equations of the wave-front are worked out for the special case of the reflection of a plane wave at a spherical mirror, and a method of drawing the shadow-forms is described. The equations to the shadows for this case are given in polar and Cartesian forms, and discussed in detail. The paper concludes with an account of the methods adopted for obtaining photographic records, and of a method for viewing the forms directly by replacing the luminous point by the eye. Three experiments were shown to illustrate this last point, as well as a number of the photographs obtained.

Dr. W. WATSON expressed his interest in the paper, and said that the diagrams shown proved that when dealing with problems similar to those considered in the paper, it was better to deal with wave-fronts rather than with rays. In his opinion, the subject of aberrations in lenses was one which should be more frequently studied by students. It was possible to illustrate many important facts by the use of cheap and simple apparatus.

The CHAIRMAN supported Dr. Watson in his remarks with reference to the advantages of dealing with wave-fronts instead of rays in the consideration of optical problems. He impressed upon the meeting the necessity of a more careful study of aberrations and image-formations, stating that papers similar to that read by Mr. Bennett could not fail to be of practical importance in the optical industry.

Messrs. W. G. PYE and Co., of Cambridge, exhibited a large quantity of apparatus manufactured at their works. The exhibit included:—

A new Compound Reading-Microscope, capable of being used in four positions.

A large Combination Spectrometer and Spectroscope on somewhat new lines, all motions and fittings arranged geometrically.

A large Cathetometer.

Tudsbury's Pneumatic Influence Machine, working in compressed CO₂ giving a thick 6-inch spark.

NOTICES OF BOOKS

Microscopic Analysis of Metals. By FLORIS OSMOND. Edited by J. E. STEAD, F.R.S., F.I.C. With 100 Photographic Illustrations and Two Folding Diagrams. London: Charles Griffin and Co., Ltd. 1904. Pp. 178.

METALLOGRAPHY, or the description of the structure of metals and their alloys, owes much to the method of "polish attack" devised by the author, and combined with polishing in bas-relief and chemical attack, furnishes reactions by which the primary constituents of carbon steels may be defined; it is to this latter object that this volume is principally devoted.

The constituents of carbon steels, apart from the slag and the graphite, are six in number, though further research may reveal others. The chief constituent is the iron itself, and considered structurally it is called "ferrite"; the second constituent is carbide of iron, and is called "cementite," and as it can be obtained in two distinct forms, the mixture is also given another name, viz., "pearlite"; the other of these forms is called "sorbite," after the first pioneer in metallography.

The fourth constituent is obtained by quick quenching in cold water from a temperature a little higher than the maximum temperature of the critical interval, and is called "martensite"; the fifth constituent has been obtained by quenching steels during the critical interval, Ar₁'₂'₃; that is to say, during the course of transformation, and is called "troostite." The sixth and last constituent is called "austenite"; this is obtained by heating the steel to above 1000°, and quenching in a bath at 0° C., or a little below; the proportion of carbon must exceed 1.10 per cent.

After fully describing these constituents and the manner of their occurrence, the author next proceeds to their micrographic identification; then follows a detailed examination of selected steels.

The final chapter deals with the theoretical and practical conclusions to be drawn from the foregoing ones. The principal theoretical conclusion was that the assimilation of quenched steel to solid solutions was placed beyond all doubt, and most convincing examples of the assimilations of solid solutions to liquid solutions were found. Practically it has been seen that the principal circumstances of the calorific treatment of steels reveal themselves in the variations of structure, with a precision that the mere inspection of fractures is far from furnishing, but the different aspects of the structure have not yet been correlated with the corresponding mechanical properties.

The practical application of metallography to metallurgists and engineers requires, therefore, a preparatory study for each metal, but we have no doubt that rapid progress will be made in this direction, so that it will be easy to determine the calorific treatment undergone by a finished article, and to see whether or not it has conformed to specified rules.

We must give a word of praise to the illustrations, which form specimens of microphotography of a high order.

The book is well printed and arranged, and is a useful contribution to metallurgical literature. There is an index.

Property in Trade Marks; being a Manual, written without the use of Legal Phraseology, on Trade Marks and their Protection. By BREWER and SON. Second Edition. London: Taylor and Francis. 1904. Pp. 134.

The ordinary books dealing with the subject of trade marks are couched in such legal phraseology that only the specialists who devote themselves to this subject are at all likely to follow their meaning.

It is to enable the users and prospective users of trade marks to gain a practical knowledge of the somewhat intricate law governing this property that this book has been written.

In addition to the general revision of this edition, two important sections have been added, comprising about sixty extra pages of information. (1) A copy of the official alphabetical list of goods, with numbers of the classes in which such goods have been placed; and (2) a chapter dealing with the danger incurred by a trader in registering his trade mark for a whole class, when he only uses it on some of the goods contained in that class.

Being a "law book" this volume is very probably open to criticism, but such criticism is not within our province; we therefore merely point out that it may be found of use, not only by traders, but also by patent agents and solicitors who have occasionally to attend to such matters.

Introduction to the Study of Physical Chemistry. By Sir WILLIAM RAMSAY, K.C.B., F.R.S. London: Longmans, Green, and Co. 1904.

This small volume is the first of a series of manuals devoted to the study of different branches of physical chemistry, which are to be published at intervals during the next few months. The editor of the series, Sir William Ramsay, has written this general historical introduction to the volumes, and the writing of the others has in every case been entrusted to authors who are specially qualified to write authoritatively on the separate branches. The plan of issuing manuals rather than one single text-book on a subject which is still in a state of peculiarly rapid development, has many obvious advantages to recommend it, the chief being the ease with which the parts dealing with those individual branches in which more rapid progress has been made can be brought up to date. This volume, in which the treatment is necessarily of a somewhat elementary nature, is eminently suited for being put into the hands of students to lay a firm foundation for the subsequent more detailed study of physical chemistry.

Praktische Übungen zur Einführung in die Chemie. ("A Laboratory Outline of General Chemistry"). By Dr. ALEXANDER SMITH. Translated into German from the Second American Edition by Prof. Dr. F. HABER and Dr. M. STOECKER. Karlsruhe: G. Braun. 1904.

In the preface to the German edition of Dr. Smith's "Laboratory Outline of General Chemistry" the translators pay a generous tribute to the American method of imparting elementary instruction in chemistry to beginners, which according to them is far superior to the German method. This useful practical book, which represents the experience of an admirable teacher, will be of great value in calling the attention of German professors to the American method, which lays great stress on the importance of practical work as a foundation for theoretical instruction. The German edition faithfully preserves the characteristics of the original, which met with a deservedly favourable reception.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by FRANZ HOFMEISTER. IV. Band, 12 Hef. Braunschweig: Friedrich Vieweg und Sohn. 1903.

The last number of the fourth volume of these *Beiträge* contains only four papers. Of these the third, by Dr.

Leopold Moll, on the artificial conversion of albumin into globulin, appears to be the most important. In it are established some noteworthy relations between the carbonates of the alkalis and ammonium salts as regards their effects upon albumin, on heating to 60° , and the whole article will be found of great interest by physiological chemists. This issue contains the index to the fourth volume, and it is only necessary to read down the titles of some of the papers in order to see how the opportunity afforded by these *Beiträge* of making public the results of many important researches has been appreciated by numbers of distinguished workers in the domain of physiological and pathological chemistry.

Traité d'Analyse des Substances Minérales. Tome Second. *Métalloïdes.* ("Treatise on the Analysis of Mineral Substances. Vol. II. Metalloids"). By ADOLPHE CARNOT. Paris: Vve. Ch. Dunod. 1904.

THE second volume of this treatise on the analysis of mineral substances is devoted to the study of the metalloids. Under the heading of each element a short description is given of its physical and chemical properties and those of its more important compounds, together with methods of determination. No detail of description is overlooked, and all the processes seem thoroughly practical, so that excellent results should be obtained if the clear and adequate directions are carefully followed. Some of the rarer and more recently discovered elements are included, such as titanium, vanadium, molybdenum, &c., which are chemically analogous to the metalloids. Though written from the point of view of pure chemistry, the book contains much that is of importance in the regions of various special industries, and all classes of chemists will be able to learn from its excellent descriptions of the simplest, quickest, and most accurate methods for the quantitative analysis of compounds of the metalloids.

Recherches sur une Propriété Nouvelle de la Matière. (Researches on a New Property of Matter"). By M. HENRI BECQUEREL. Paris: Typographie de Firmin-Didot et Cie. 1903.

THIS volume on radio-activity is divided into two parts; the first deals with the author's discovery of the radio-activity of uranium, and his investigation of the physical character of the newly found radiation; though this part is in effect an abstract of papers originally published six or seven years ago, the various observations then made are discussed in full detail in order to show better the successive stages in the progress of our knowledge of the subject. The second part contains an account of the author's work since the discovery by the Curies in 1898 of other substances exhibiting the same phenomena in a far higher degree. Since the monograph aims only at giving a full account of the author's own work, that of the Curies and others is not described as fully as would be necessary in a complete treatise, though it is by no means passed over or minimised. The volume contains some most interesting plates, and a bibliography brought up to September, 1903.

Up to Date Tables of Imperial, Metric, Indian, and Colonial Weights and Measures. Simple Suggestions for Metric Adoption; Imperial Decimal Coinage, Foreign, Indian, and Colonial Moneys; Standard Time, Mensuration, Interest; Specially prepared Maps; Metric Measurements applied to Out-door Games. By ALFRED J. MARTIN, Fellow of the Surveyors' Institute, England. London: T. Fisher Unwin.

THE author has brought together a mass of matter connected with the increasingly important subject of the introduction of the metric system, and many arguments are used in favour of its speedy adoption in weights, measures, and coinage, and suggestions are made in view of minimising the temporary inconvenience that must necessarily at first accompany the proposed change.

The author deals in a minute and thorough manner with the effects that the proposed alteration would have upon various trades and professions, and strongly emphasises the absurdity of continuing our present system and the advantages that would follow the change.

The book includes also much information only indirectly connected with the subject, such as examples on the use of logarithms, the Morse code, astronomical symbols, signs of the Zodiac, &c.

Supplementing the above comprehensive work the author has issued a small fifty page penny "Table book" for use in schools, showing how decimals can be taught at a very early age, and containing many original ideas and hints upon the introductions of the elementary principles of the subject. Both books are well printed and of handy size, and will be found of value to both commercial and professional men.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

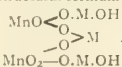
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxviii., No. 8, February 22, 1904.

Direct Hydrogenation of Aniline. Synthesis of Cyclohexylamine and two other New Amines.—Paul Sabatier and J. B. Senderens.—The general method of direct hydrogenation by reduced nickel can be applied to aniline. If aniline vapours containing excess of hydrogen are passed over nickel at a temperature of about 190° an intense absorption of gas takes place, with evolution of ammonia. An almost colourless liquid condenses with a pronounced ammoniacal odour. This liquid contains, besides a small quantity of non-transformed aniline, three amines present in almost equal quantities:—(1) Cyclohexylamine, $C_6H_{11}NH_2$, boiling at 134° ; (2) dicyclohexylamine, $(C_6H_{11})_2NH$, boiling at 250° ; (3) cyclohexylaniline, $C_6H_5NHC_6H_{11}$, boiling at 275° .

Experimental Researches on Distillation.—Eug. Charabot and J. Rocherolles.—Unsuitable for abstraction.

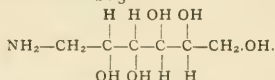
Alkaline Earth Manganate-manganates.—V. Auger and M. Billy.—The authors re-investigate the alkaline earth manganates, and find—(1) That none of the products hitherto obtained by the recognised methods possess the formulæ of manganates, but that all contain a less quantity of oxygen than that demanded by the formula $MMnO_4$; (2) that Dulaurier's calcium manganate is only a mixture of lime, manganese dioxide, and calcium manganite. The authors obtain the above products as pure as possible by melting together, at temperatures varying from 180° to 250° , mixtures of potassium permanganate, the alkaline earth base, and a fusible mixture of alkaline nitrates. Oxygen is evolved, and a green mass obtained, which, when treated with suitable solvents, leaves a blue-green powder, insoluble in water, and which, on analysis, is found to possess the formula $Mn_2O_8M_3 \cdot H_2O$, which can be developed into the structural formula—



This can be considered as a compound of a manganite and a manganate, i.e., a mangani-manganate. The authors specially examine barium mangani-manganate.

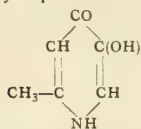
Action of Carbon Dioxide on Solutions of Sodium Nitrite.—Louis Meunier.—The author proves that in Marie and Marquis's experiments on the action of carbon dioxide on sodium nitrite, the large quantity of nitrous acid set free is exclusively due to the presence of potassium iodide.

Mannamine : a New Base derived from Mannose.—E. Roux.—The author finds that the reduction of mannose gives a new base (mannamine), which represents amino-1-hexanepentol. $\frac{4.5}{2.3} . 6 : -$

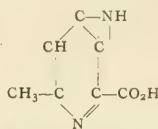


He also describes the properties of the new base and certain of its salts.

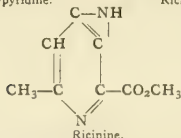
Ricinine.—L. Maquenne and L. Philippe.—The reactions given by ricinine, which the authors describe, show that ricinic acid is probably the carboxyl derivative of an iminomethylpyridine. From this they evolve the formulæ of ricinine and the products of decomposition to be cyclic products as follows :—



Methylpyridine.



Ricininic acid.



Ricinine.

Inversion of Sugar.—L. Lindet.—The author performs a series of experiments which control and generalise the inversion of sugar. He finds that when sugar solutions are heated in metallic vessels, the hydrates play an important part in the inversions. If the liquid is aerated, inversion is more active than if the liquid has been previously boiled. An aluminium vessel gives more or less strong inversion, because the sides become covered with alumina, which is a very active agent.

Simultaneous Existence in Living Cells of Oxidising and Reducing Diastases.—E. Pozzi-Escot.

MISCELLANEOUS.

American Electro-chemical Society.—The fifth meeting of the American Electro-chemical Society will be held at Washington on April 7th, 8th, and 9th, 1904. The meetings will be held at the Columbian University. Thursday and Friday afternoons will be devoted to visits to scientific laboratories, Government Institutions, and various points of interest in and about Washington; on Thursday evening the Presidential Address will be delivered, and will be followed by a Smoking Concert; on Friday evening there will be a Subscription Banquet. A number of papers are announced to be read, and others are expected, and the attention of members is called to the A. B. Frenzel Prize of 250 dollars, the conditions of which are stated on p. 10, vol iii., of the *Transactions*.

The "Bastian" Mercury Vapour Lamp.—On Saturday afternoon last, March 19th, a private exhibition was given at the offices of Messrs. Rumney and Rumney, 39, Victoria Street, Westminster, of the new "Bastian" Mercury Vapour Lamp. The light given by this lamp closely resembles that of the moon, and will no doubt be well adapted for street lighting; we do not consider it would be a comfortable light for interiors as it is too

"ghostly" in its effects. The light is produced by means of a long arc passing through an exhausted glass tube saturated with mercury vapour; in this respect it resembles other mercury vapour lamps, but it has this advantage, that though the voltage may vary as much as 50 per cent, the lamp burns steadily on, only the quantity of light is reduced as the length of the arc decreases, the quality remaining the same. The "Bastian" lamp is at present adapted for continuous currents only, but we are informed that it is expected before long to get them to work on an alternating current. It is extremely simple in construction, and there is nothing to get out of order, no filament to break, and no carbons to burn up, while the efficiency claimed is 2½ candle-power per watt; each lamp requires anything from 40 to 60 volts and about 0.7 ampère, or the same as an incandescent lamp of 8-candle power, while the light given is no less than 80-candle power, or ten times as much. The colour difficulty, owing to the absence of red rays, is claimed to have been overcome (at a slightly increased cost) by one of the numerous patents taken out by the inventors.

CROOM & CO.

COPPER OVENS & BATHS.

Accurately constructed to Customers' requirements.

Estimates free by return of post.

MAKERS TO THE TRADE.

75, LEADENHALL STREET, E.C.

THE CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 20 words to line)	0	3	6
Each additional line	0	0	6
Whole column	1	15	0
Whole page	3	0	0

A reduction made for a series of insertions.

Cheques and Post Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

M I C A.

Telephone
No 248
Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E.C. & London.
MICA MERCHANTS
Manufacturers of Mica Goods or Electrical and ALL purposes.
Contractors to His Majesty's Government

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

suggested on best terms by
WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widdow.
LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.

THE CHEMICAL NEWS.

Vol. LXXXIX., No. 2314.

THE EXISTENCE OF HYDRATES IN CONCENTRATED AQUEOUS SOLUTIONS OF ELECTROLYTES.

By HARRY C. JONES

and
FREDERICK H. GETMAN (Carnegie Research Assistant).

In our paper published in the Ostwald "Jubelband" (*Zeit. Phys. Chem.*, 1903, xlv., 244), we gave considerable data which seemed to point to the correctness of the suggestion made three years before by Jones and Chambers (*Am. Chem. Journ.*, 1900, xxiii., 89), that in concentrated solutions of electrolytes the dissolved substance is combined with a part of the water forming hydrates. This suggestion was originally put forward by Jones and Chambers to account for the fact that such solutions of electrolytes give abnormally great lowerings of the freezing-point of water.

When the work recorded in the Ostwald "Jubelband" was finished, we had studied thirty-four compounds—acids, bases, and salts—and had found, in practically every case, abnormally great lowering of the freezing-point of water; if we take as the normal lowering that calculated from the dissociation. We also pointed out (*Zeit. Phys. Chem.*, 1903, xlv., 286) that such solutions of electrolytes give abnormally great rise in the boiling-point of the solvent, and further, that the minimum in the boiling-point curve was at a greater concentration than in the freezing-point curve. This was in accord with our suggestion of the existence of hydrates in such solutions, since the hydrates formed would be less stable at the higher temperatures, and therefore greater concentration would be necessary for their formation in quantity or complexity sufficient to change the direction of the curve.

Since the above work was done, fifteen other salts have been studied in this connection. They are the chlorides, nitrates, and sulphates of manganese, nickel, cobalt, copper, and aluminium. All of these substances show abnormally great lowerings of the freezing-point of water, except two or three sulphates, which we proved were polymerised in such solutions. Aluminium chloride and nitrate gave very great lowerings of the freezing-point of water—the former giving in the most concentrated solution studied, a lowering which was nearly five times as great as the calculated value. These results will be published and discussed in full in the April number of the *American Chemical Journal*. Most of these substances also show minima in the freezing-point curves, but this is of subordinate importance.

The point upon which we wish to lay stress in this brief communication is the relation between the water of crystallisation of a compound and the magnitude of the freezing-point lowering in concentrated solutions. If electrolytes form hydrates in concentrated solutions, it is only reasonable to expect that, of correlated substances, those that crystallise with the most water will be the substance that will combine with most water in such solutions, will show the greatest amount of hydration. This can be readily tested, since those compounds which, in solution, combine with the greatest amount of water would be the compounds that would produce the greatest lowering of the freezing-point. This is obvious, since the water that is combined with the dissolved substance no longer plays the rôle of solvent, and is removed from the field of action as far as freezing-point lowering is concerned. That such a relation, in general, exists we shall show in our next communication in the *American Chemical Journal*. It can, however, be seen for the chlorides of the alkalis and alkaline earths (*Zeit. Phys. Chem.*, 1903, xlv., 281, Fig. 3), that they stand in the same relation with respect to the

amount to which they lower the freezing-point of water in concentrated solutions, and with respect to the water of crystallisation. The three alkali chlorides, sodium, ammonium, and potassium, have no water of crystallisation, and all lower the freezing-point of water to about the same extent. Lithium chloride, which crystallises at low temperatures with two molecules of water, gives considerably greater lowering of the freezing-point than the alkali chlorides. When we turn to the chloride of the alkaline earths, we come first to barium chloride, which has, under normal conditions, two molecules of water. It gives much greater lowering than even lithium chloride. This, however, is just what is to be expected, since barium chloride crystallises with water under conditions where lithium chloride crystallises with no water. Further, it is a ternary electrolyte, while the chlorides of the alkalis are all binary electrolytes. Barium chloride could not be studied at any great concentration on account of its limited solubility. Strontium chloride and calcium chloride each crystallises with six molecules of water. They show considerably greater lowering than barium chloride.

If we turn to the bromides of the alkaline earths, exactly the same relations appear as with the chlorides, as is evident from the work of Jones and Chambers (*Am. Chem. Journ.*, 1900, xxiii., 96). Comparing Figs. 1 and 2 (*Ibid.*), we find that magnesium chloride, with six molecules of water of crystallisation, gives greater lowering than calcium chloride with six molecules of water, and this in turn gives greater lowering than strontium chloride with six molecules of water. Strontium chloride gives greater lowering than barium chloride with two molecules of water.

Turning to the bromides, magnesium bromide with six molecules of water gives greater lowering than calcium bromide with six molecules of water. Calcium bromide, in turn, gives greater lowering than strontium bromide, which also has six molecules of water of crystallisation. Barium bromide with two molecules gives less lowering than even strontium bromide. The relations between the chlorides and bromides are thus perfectly satisfactory.

If we turn to the nitrates of the alkalis (*Zeit. Phys. Chem.*, 1903, xlv., 281, Fig. 4), we find that lithium nitrate, with two and one-half molecules of water of crystallisation, gives much greater lowering than the nitrates of sodium, ammonium, and potassium, which have no water of crystallisation, and which give about the same lowering of the freezing-point of water.

When we turn to the sulphates of the alkalis, they all give about the same lowerings of the freezing-point, and only sodium sulphate crystallises with water of crystallisation. The amount of water with which sodium sulphate crystallises is a function of the conditions under which it crystallises, and from the nature of the resulting compounds it is questionable whether it holds any water in stable equilibrium.

The carbonates of the alkalis present the only possible exception to our generalisation of the thirty-eight substances that we have thus far studied that have water of crystallisation. Sodium carbonate under ordinary conditions crystallises with more water than potassium carbonate, and gives somewhat smaller lowering of the freezing-point of water. Sodium carbonate, however, readily loses a part of its water of crystallisation when it crystallises with ten molecules of water; and further, can be readily obtained from solution, by varying the conditions under which it crystallises, with seven molecules of water, with five molecules of water, with two molecules of water, and with one molecule of water. The apparent exception presented by these two carbonates is, then, not as well defined as might at first appear. A large number of similar relations exist among the fifteen substances that we have studied since our paper was forwarded to the Ostwald "Jubelband," but these will be seen when our paper is published in the *American Chemical Journal* in April.

It may be said, in general, that of the thirty-eight compounds studied containing water of crystallisation, there is

scarcely a well defined exception to the generalisation, that the molecular lowering of the freezing-point, in concentrated solutions of substances that are closely related chemically, is a function of the number of molecules of water with which the substances crystallise.

We regard this relation as a strong argument in favour of our theory of the existence of hydrates in concentrated solutions of electrolytes. It is well known that many non-electrolytes also give abnormally great lowering of the freezing-point of water in concentrated aqueous solutions. This is probably due to the same cause. It is probable that such substances also form hydrates in concentrated solutions. We shall take this problem up systematically in the near future.

The theory of the existence of hydrates in concentrated aqueous solutions is probably a general theory of such solutions. Of the forty-nine substances that we have thus far studied, all except a few sulphates, which we have proved undergo polymerisation in such solutions, show abnormal freezing-point lowerings in concentrated solutions. Some show a value only a little greater than the value calculated from their dissociation. These are the substances that crystallise with no water of crystallisation, or with very little water of crystallisation. Others show a value for the molecular lowering that is two or three times the calculated value, while others still, such as aluminium chloride and nitrate, with as large amount of water of crystallisation as that possessed by any chloride or nitrate studied, and which are quaternary electrolytes, show even greater lowering as compared with the calculated value. These and many other relations are fully developed in our next paper to which reference has already been made.

We think we have experimental evidence for the existence of hydrates in concentrated solutions of nearly all the substances that we have studied. This is the first time that direct evidence for the existence of hydrates, in general, in concentrated aqueous solutions has been furnished.

The importance of this fact for physical chemistry is very great indeed. It has been said, and justly said, that the relations between gases and solutions, of which the physical chemists make so much, apparently hold only for very dilute solutions. The reason why these relations apparently do not hold in concentrated solutions is that, in such solutions, the dissolved substance combines with a part of the solvent, forming hydrates with it, and thus diminishes the amount of solvent present, acting as such.

When these hydrates are taken into account it is more than likely that the gas laws will be shown to hold for concentrated solution as well as for dilute; especially if the gas laws are applied to concentrated solutions as to concentrated gases, in accordance with the equation of Van der Waals.

Having established, to our own satisfaction at least, the existence of hydrates in concentrated solutions of electrolytes, we calculated the composition of such hydrates in a number of cases. We find that the most concentrated solution contains the most complex hydrate, just as we would expect, since dilute solutions cannot contain hydrates of any appreciable complexity, as is proved by the fact that the freezing-point method and the conductivity method of measuring dissociation give the same results. We have also calculated the composition of the hydrates formed by a given substance at various concentrations, and have plotted the results in a curve—one ordinate being the composition of the hydrate, and the other the concentration of the solution. To our delight every substance thus dealt with gave a perfectly smooth curve, notwithstanding the fact that every point on the curve contained four experimentally determined values.

These facts will all appear when our paper (*Am. Chem. Journ.*, April, 1904) describing this work in full is published in the near future.

Chemical Laboratory,

Johns Hopkins University, Baltimore, U.S.A.
January, 1904.

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.*

A STUDY OF NEODYMIUM: PREPARATION OF PURE MATERIAL—EFFORTS TO DECOMPOSE IT INTO ITS CONSTITUENTS.

By CHAS. BASKERVILLE and RESTON STEVENSON.

Synopsis.—This paper presents a new and rapid method of freeing neodymium from lanthanum, viz., fractional precipitation of the chloride solution by saturation with gaseous hydrochloric acid. A number of fractionations of the purified material were made to prove the complexity of neodymium, but without success. The methods used were, fractional precipitation by gaseous hydrochloric acid (over 100); partial decomposition by fusion of the double alkaline nitrates (23); precipitation by primary ammonium oxalate (31); solution in ammonium carbonate and precipitation with acetic acid (3); fractional precipitation by such organic bases as aniline (4), benzylamine (29), piperidine (19), and phenylhydrazine (8).

Naturally investigations were to be carried along with the foregoing, looking toward the preparation of pure neodymium compounds. It was noted that the preparation of pure neodymium salts, according to Auer's method, presented numerous difficulties, and required much time and many repetitions of the process. Boudouard (*Comptes Rendus*, cxxvi., No. 12; *CHEMICAL NEWS*, lxxvii., 193) has shown that neodymium gives a double sulphate with potassium more soluble in water than that of praseodymium, and presents a more rapid separation than is perhaps possible by fractional crystallisation. Muthmann and Rolig (*Ber. d. Chem. Ges.*, 1898, xxxi., 1718—1731), working with didymium, had from yttria, extracted from monazite sand, found, after making sixty crystallisations, a neodymium sulphate containing only 0.3 per cent of praseodymium. The oxide, Nd_2O_3 , obtained by them was described as "fast weiss"—(see below).

Reference has been made to the tentative acceptance of neodymium as an element. The agreement of the figures given for the atomic weight of neodymium by Jones (*Am. Chem. Journ.*, xx., 345), Brauner (*Proc. Chem. Soc.*, 1898, No. 191, p. 70), and von Scheele (*Zeit. Anorg. Chem.*, xvii., 310) point clearly to a constant material obtained from different sources. The same was also true of didymium before the classical work of Auer von Welsbach (*loc. cit.*). Urbain (*Bull. Soc. Chim.*, [3], xx., 9; *CHEM. NEWS*, lxxviii., 74), in studying didymium, had from yttria extracted from monazite sand, found not only neodymium, but such other earths as erbium and Soret's X (holmium), members of the terbic group and a little cerium. While absorption band 469 was distinctly visible, 482 and 444 were doubtful (see papers following). Demarcay (*Comptes Rendus*, civ., 580) and Krüss and Nilson (*Ber. d. Chem. Ges.*, xx., 2124) had previously made analogous observations with variations of the relative intensities of these bands. Later, Demarcay (*Comptes Rendus*, cxvii., 14; *CHEMICAL NEWS*, lxxvii., 219) showed that some absorption bands have been found in didymium which appear to belong neither to neodymium nor praseodymium. Further, the presence of a certain amount of samarium causes the blue bands to disappear in a vague, hardly visible nebulosity. He concluded, as a result of a number of fractionations by different methods and examinations of the absorption bands, spark spectra (including the ultra-violet region), fluorescent spectrum in calcium sulphate, and by spectral colorimeter, "in spite of statements of several chemists, neodymium is a simple body and not a mixture." Yet the work by Brauner (*Proc. Chem. Soc.*, March 31, 1901) on variations in the oxides gives evidence of the complexity of that element.

* Presented in abstract at the Cleveland Meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, 1904, xxvi., No. 1.

Our investigation was begun with the intention of testing the nature of neodymium. Many have difficulty in assigning neodymium a satisfactory location in the periodic system. Therefore, in the event we learned that neodymium was simple, it was highly desirable to determine positively its place in the natural system.

Obviously the first step was to prepare neodymium as pure as possible. The constant associates of neodymium are lanthanum and praseodymium, which are separated by methods which, at best, are long, slow, and difficult of execution. It is very desirable, therefore, to secure a method thorough and quick for the absolute elimination of these accompanying substances.

500 grms. of crystalline, double ammonium neodymium nitrate were used during the preliminary trials of different methods.*

Partial Decomposition of Double Nitrates by Fusion.

The classic method of Berlin (*Scand. Naturf.*, 8 *Möde Köpenhamn*, 1860, p. 448) was applied to 200 grms. of the ruby-coloured crystals which had lanthanum as the main impurity and some praseodymium. The numerous variations of the directions given by Berlin, offered by subsequent workers, looking toward uniform heating and decomposition, failed to improve the process. At best, such methods of fractionation required a great amount of time and patience. The material was carried through twenty-three fractionations, and, while much of the lanthanum was removed, the neodymium still contained praseodymium.

Hood (*CHEMICAL NEWS*, lii, 271), discussing principles of fractioning, observed:—"It is evident then that fractional precipitation is a method for separating two oxides differing but slightly in basic properties. It may be the work of a lifetime, even when working on a large amount of material." Having the latter and not being assured of the temporal allotment of a chemist (thirty years), we looked for more encouraging methods.

Saturation of Neodymium Chloride Solution with Hydrochloric Acid.

The neodymium ammonium nitrate containing lanthanum as chief impurity with some praseodymium was converted into the chloride by the precipitation as hydroxide with ammonia, and washing free of the precipitant. It is inadmissible to convert the double salt to the oxide by direct ignition in platinum, as the metal is attacked. To be sure, it would appear that this contamination could be readily removed by subsequent solution of the oxide in hydrochloric acid. In practice, however, the platinum is found in the solution. The explanation of this is easily had. In the first place, Brauner (*Proc. Chem. Soc.*, March, 1901; *CHEMICAL NEWS*, lxxiii., 197) has shown the formation of a dioxide when the nitrate is ignited. This oxide causes the evolution of chlorine on dissolving it in hydrochloric acid with the consequent solution of the platinum. In the second place, the metal is finely divided, and W. L. Dudley (*Journ. Am. Chem. Soc.*, 1893, xv., 272) and Mallet (*Am. Chem. Journ.*, 1901, xxv., 430) have shown that platinum in this condition and exposed to the air is soluble in hydrochloric acid. In later work, where large quantities were used, large earthenware tubs of 100 litre capacity with a spiral row of decantation openings on one side were used. The hydroxide was allowed to settle and supernatant liquid drawn off, and the hydroxide washed twice with water by decantation. The decantations were filtered free of any suspended hydroxide, and the filtrate discarded.

It may be well here to call the attention of those beginning work on the rare earths to the advisability of pursuing the very safe plan of saving all filtrates until they are thoroughly tested. These filtrates were not thrown away unless 10 to 20 litres had been evaporated and ignited,

and showed only a trace of residue. In many cases the clear water became turbid on standing exposed to the air. This was no doubt due to the absorption of carbon dioxide, which caused the precipitation of the neodymium compound or solution of the hydroxide in the wash-water and subsequent precipitation on neutralisation by the excess of ammonium hydroxide in the filtrate. The hydroxide was thrown upon a filter, dried, and ignited. The unglazed porcelain filter was eventually utilised in this work, as with the praseodymium, giving most satisfactory results.

The dried hydroxide was ignited in platinum over powerful Bunsen burners until no more fumes arose. The ignited product was pulverised in an agate mortar, and added to the concentrated hydrochloric acid in large porcelain casseroles. The solution, which was facilitated by heat, exhibited dichroism, presenting the colour of juniper swamp water (yellowish brown) with transmitted light, and purple with reflected light (especially noticeable upon pouring), and faintly purple on dilution.

The neodymium chloride was filtered to remove a small grey residue of platinum obtained from the vessels, and concentrated until a crust of crystals formed on top of the solution. On cooling, yellow-brown crystals appeared abundantly. They were separated, dissolved in water, and the mother-liquor of neodymium chloride separately fractionated by saturation with hydrochloric acid gas.

This method of treatment possesses nothing essentially new, having been fully described previously by Dennis (*Journ. Am. Chem. Soc.*, 1902, xxiv., 421, and previously). The gas was generated by allowing concentrated hydrochloric acid to fall dropwise upon concentrated sulphuric acid. The generator was provided with a safety-flask, and the gas let into the solution by means of an inverted funnel or thistle tube, which just dipped underneath the surface of liquid.

During the early work and with the small quantities of material, only pure acids were used. When, however, later, large quantities of material (several carboys of acids) were employed, on account of the expense, commercial reagents were had recourse to. A satisfactory generator of gaseous hydrochloric acid from commercial acids was devised by one of us (Stevenson), and W. M. Marriott (of this laboratory), and is described elsewhere.

The solution was saturated with the gas until crystals appeared. The supernatant liquid was carefully decanted, the crystals washed with concentrated chemically pure hydrochloric acid, and the liquid again decanted from any crystals which subsequently formed in the mother-liquor. It was later learned that by allowing the solution to cool, the two crops of crystals could be collected in the one beaker, and washed several times with hydrochloric acid; the mother-liquor was subjected to another fractionation, crystals re-dissolved in the least amount of water, and fractionated again. Whenever solutions became too weak to be further fractionated, they were concentrated, and subjected to the action of the gas.

During the earlier part of the work, forty-five fractionations were made, and the resulting fractions classified according to the absorption spectra into four large solutions; the extreme crystals, medium crystals, medium solutions, and extreme solutions, and into two small solutions—the pene-extreme crystals and the pene-extreme solutions. These solutions were fractionated as before, except that the application of the gas was continued until no more crystals appeared, and the "criss-crossing" preceded each fractionation.

After twenty-two more of such fractionations, there resulted four fractions:—Extreme crystals, a very large fraction; medium crystals, about two-thirds as large; medium solutions, a moderate-sized fraction; and extreme solutions, small fraction. The extreme crystals in neutral nitrate solution showed an absorption spectrum identical with the spectrum of the extreme solution, except that in the latter the band λ 460–466 had disappeared. This band belongs to samarium. The arc spectrum of the oxide from the extreme crystals showed only vanishing traces of

* Obtained through the generosity of Dr. H. S. Miner, chemist of the Welsbach Lighting Co.

lanthanum.* The oxide of the extreme solution was brown and violet. The brown portion was largely lanthanum and neodymium with some praseodymium. The method therefore was promising, as almost pure neodymium was obtained in the heads.

It may be well to state the result of some of our observations here for the guidance of others in the application of this method. The method was improved as follows:—The concentrated neodymium chloride solution was saturated with hydrochloric acid gas until no more crystals appeared. These crystals were then dissolved to a saturated aqueous solution, and refractioned. After seven such complete precipitations, the last crystals were absolutely free from lanthanum, according to the arc spectrum. This method was used on a large scale subsequently, working with as much as 8 kilograms of neodymium ammonium nitrate, using the hydrochloric acid generator of Stevenson and Marriott. Within a week, a kilogram of neodymium oxide absolutely free from lanthanum was obtained. This serves to illustrate the value of the method.

Remarks.

During all our investigations with the rare earths, on account of their value, the fragile containers are always placed in a second large vessel in case of accidental breakage.

The precipitation with the hydrochloric acid gas sometimes began immediately, generally in about twenty minutes. In a few cases, where the solution was dilute, only after two hours, and in a few very dilute solutions not at all. The mother-liquor decanted from crystals frequently yielded another crop on standing. Oftentimes, apparently, a supersaturated solution would be had which, when poured from one vessel to another, gave rise to spontaneous crystallisation.

The precipitates were always crystalline. Rapid precipitation from saturated solutions gave trellised translucent crystals which appeared white in the mother-liquor. Vitreous needles resulted from the concentrated solutions; fine iridescent crystals from dilute solutions. The spontaneous crystals, especially when formed after days of standing, were handsome pyramids from 4 to 7 m.m. in length. The crystals were always more or less coloured; the extreme crystals were redder, and the crystals from the extreme solutions were yellowish. Sometimes the crystals appeared in alternate layers of rose and white, very likely due to a different manner of precipitation, because no difference was observed in the absorption spectra of solutions made from the two. This is no proof, however, that different substances did not separate out more or less contaminated with each other, for, as is well known, the absorption spectrum is not a final test of a fractionation.

These observations were made near the time when it would become necessary for one of the authors (S.) to leave this laboratory, so that checks could not be made by means of atomic weight determinations. This work will be taken up later.

The colours of the solutions obtained in the fractionations were striking. The characteristic dichroism of the original chloride solution has been adverted to. The extreme solutions were a bright yellow in transmitted light, and bright green in reflected light. The criss-crossing was determined by the colour of the solutions; and the classification by colour, location in the chart of the fractionations, but mainly by the absorption spectra. All these methods agreed.

The absorption spectra at first were taken of fractions as obtained without any attempt at uniform concentration. As a result, the spectra were deceptive, and not comparable. Subsequently a basis was assumed for all comparisons, 1 grm. of oxide being converted into neutral chloride and diluted to 10 c.c. An interesting observation was made in

the examination of the fractions by means of the absorption spectrum, for band λ 460–466, the strong band belonging to samarium, according to Thalen, disappeared coincident with the loss of the yellow purple dichroism.

The bands λ 569, 482, 469, and 443, characteristic of praseodymium, persisted throughout; yet, according to the arc spectrum, the praseodymium was present in a very small amount—less than 1 per cent as shown by Jones (*Am. Chem. Journ.*, xx., 345). We were so fortunate as to have in our possession some of the material used by Dr. H. C. Jones in his careful atomic weight determinations of neodymium and praseodymium. The arc spectrum of the purest preparation showed traces of gadolinium and samarium in both samples, but by a comparative examination of a solution of samarium, the absorption lines of this element were not found as impurities in our purest neodymium.

The colour of the oxides obtained from the different fractions presented an interesting study. Demarcay (*Comptes Rendus*, cxvii., 14; *CHEMICAL NEWS*, lxxvii., 219) states that pure neodymium is a violet-coloured oxide. A pale violet oxide was given by the extreme crystals, but a lump of it had a brown core, which easily became violet upon ignition (compare Muthmann and Rölzig above). This same oxide upon recovery after use for precipitation by organic bases (see below) was a mixture of brown cinders, rose-coloured scales, mole-skin dust, and black specks; yet each of these, carefully picked out and separately examined, gave the same absorption bands—the true spectrum of our purest neodymium. The oxides of the extreme solutions was a mixture of lavender and brown. It sometimes became almost white upon vigorous ignition, indicating the predominance of lanthanum. Certain blue oxides were also obtained, and when sufficient shall have accumulated, will be examined (see *Journ. Russ. Phys. Chem. Soc.*, xxix., 209). Perhaps this may prove to be Chroustschoff's glaukodymium. The dark oxides go into solution in nitric acid more energetically than the lavender-coloured oxides, a temporary rose-coloured residue being obtained.

Further Experiments looking to Proof of Complexity of Neodymium.

Having secured pure neodymium containing only a trace of praseodymium, we applied a few methods looking toward a determination of the nature of that element. Below are given the methods used.

Precipitation by Primary Ammonium Oxalate.

A neutral neodymium chloride solution prepared from the pure oxide obtained according to the method given above was used. A saturated aqueous solution of ammonium oxalate was added until a permanent cloudiness was obtained. About 5 c.c. of saturated primary ammonium oxalate was then added, giving local turbidity, which became a mealy precipitate upon stirring. This was essentially the method used by Dennis and Dales in their work upon the purification of yttrium (*Journ. Am. Chem. Soc.*, 1902, xxiv., 425). After twelve hours, the precipitate settled as a rose-coloured powder, leaving the supernatant liquid clear. Thirty-one such fractionations were made. The last two fractions were obtained as follows:—To the boiling mother-liquor 10 c.c. of the primary oxalate were added, and no precipitate formed, but on cooling, crystals gradually appeared. The plan of adding praseodymium oxalate crystals to induce a separation of that constituent of didymium was tried, but the solution was exhausted. The final mother-liquor was evaporated to dryness, ignited, converted into neutral chloride solution, and examined with the spectroscope. All of the mother-liquors obtained throughout the fractioning were similarly treated, as well as the precipitates. The same absorption spectrum was obtained in every case; therefore, the process was not tried more elaborately.

* These determinations were made by Dr. W. J. Humphreys, of the University of Virginia, with the same instrument as mentioned in the Praseodymium paper.

Solution in Ammonium Carbonate and Precipitation by Acetic Acid.

Pure neodymium hydroxide obtained from the chloride above by precipitation with ammonia, was washed twice by decantation. 400 c.c. of water saturated with pure ammonium carbonate were added. No perceptible solution of the hydroxide was observed. The liquid was poured off and the hydroxide washed three times by decantation. The liquid gave no precipitate with acetic acid, but on evaporation and ignition a very small residue was obtained. Converted into a neutral chloride solution, the liquid showed only the stronger absorption bands of neodymium. It was too small in amount to be made up to the standard strength adopted. The neodymium hydroxide was treated once more with 300 c.c. of saturated ammonium carbonate or several days with a similar result, consequently it was abandoned.

Fractional Precipitation by Organic Bases.

G. Krüss (*Zeit. Anorg. Chem.*, 1893, liii., 108) fractionated certain of the rare earths with such substituted ammonias as aniline. Smith and Jefferson (*Journ. Am. Chem. Soc.*, 1902, xxiv., 540) published the effect of precipitating the rare earths with aromatic bases. We endeavoured to utilise their observations in making fractional precipitations similar to the work of Schutzenberger and Boudouard, and other workers in fractionating the rare earths with ammonia. E. T. Allen later used certain weak organic bases for separating thorium and zirconium from iron and beryllium (*Ibid.*, 1903, xxv., 421).

Aniline.—To a moderately concentrated, slightly acid solution of neodymium chloride, aniline was added in excess, with stirring. No precipitate appeared at once. The solution was concentrated, and more aniline added. After three days, a slight white precipitate formed, adhering to the beaker. It was filtered, and the filtrate treated with aniline, and boiled. More aniline was added, and another meagre white precipitate formed. Further attempts to get a larger precipitate, even after allowing the solution to stand for three months, failed. These three precipitates showed similar absorption bands, and were identical with the spectrum of the diluted mother-liquor. The process was unpromising, and therefore discontinued.

Benzylamine.—Benzylamine upon addition to a neutral neodymium chloride solution immediately gave a rose-coloured, flocculent precipitate, the liquid becoming somewhat cloudy upon stirring. The precipitate settled after twelve hours, and was very difficult to filter. Only eight drops of the organic base were used to get a fractional precipitation, because, as stated by Smith and Jefferson, the precipitation is quantitative (*loc. cit.*). After twenty-nine fractionations, the solution was exhausted. Spectroscopic examination of the precipitates, the mother-liquors, and the final residue, according to the methods already cited, showed nothing noteworthy, and the process was not further elaborated.

Piperidine.—Piperidine acted similarly to benzylamine, nineteen fractions being carried out. The mother-liquor soon assumed a bright yellowish green colour. Some of the hydroxides were rose colour and some were almost pale yellow.

Phenylhydrazine.—The phenylhydrazine was added in an excess to a neutral chloride solution. Gradually, in the course of twenty-four hours, there formed a dark red precipitate which adhered to the beaker, and was difficult to filter. The precipitate was dissolved in concentrated nitric acid, and gave a dark red solution due to the action of the acid upon the organic base, or a decomposition product of the base. Seven fractionations, each one requiring a week, were carried out. The precipitates showed no divergence from the original, when in the form of neutral chloride solutions they were examined with the spectroscope. After the third precipitation, the filtrate became so turbid, either from decomposition products of the phenylhydrazine, or through hydrolysis of such double compounds

as are mentioned by Delafontaine, that the process was given up.

Summary.

In endeavouring to prove the complexity of neodymium by fractional precipitation, in our hands the following methods failed:—Fusion of the double nitrate, according to Berlin (see preceding paper); precipitation by primary ammonium oxalate; solution in ammonium carbonate and precipitation by acetic acid; fractional precipitation by gaseous hydrochloric acid; precipitation by the organic bases—aniline, benzylamine, piperidine, and phenylhydrazine.

The following methods are among those which will be tried in this laboratory:—The use of sodium acetate and hydrogen peroxide, electrolysis, reduction by metallic magnesium, magnesium usta, treatment with mercury oxide and nitrate, copper oxide (method applied by Schutzenberger and Boudouard to cerium), dialysis, and ammonium persulphate.

NEW FORMS OF PIPETTES.

By B. M. MUKERJEE.

I HAVE been using several forms of pipettes for drawing bromine, chlorine water, &c., which I have not seen described anywhere. The following descriptions may be useful.

The pipette, Fig. 1, consists of a reservoir, A, containing water; a tube, B, with a bulb, b, of about the same capacity

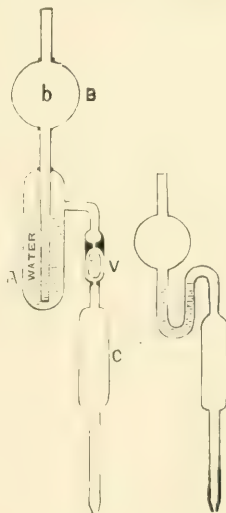


FIG. 1.

FIG. 2.

as the reservoir, passing nearly to the bottom of the reservoir; and a pipette, C. For greater safety a valve, V, is attached to the pipette, as shown in Fig. 1; it is, however, often omitted. On drawing the water into the bulb, b, the liquid rises in the pipette, C, without the fumes coming in contact with the mouth.

A simpler form of the above is shown in Fig. 2, where the U-tube serves the purpose of the reservoir in Fig. 1. This form is not quite so convenient as the other.

Thomson College, Roorkee

THE ELEMENTS: VERIFIED AND UNVERIFIED.

By CHARLES BASKERVILLE, Ph.D., F.C.S., Smith Professor of General Chemistry, University of North Carolina.
(Continued from p. 151).

LIST OF PROPOSED CHEMICAL ELEMENTS (continued).

Date.	Name.	Source.	Authority.	Reference.	Remarks.
1842	<i>Didymium</i> .	Lanthana.	Mosander.	Liebig's Ann. Chem., 44, 125; and 48, 210.	Doubted by Hermann (Journ. Prakt. Chem., 1845, 34, 182). Shown to contain samarium; later split into neo- and praseodymium by Auer (Monats., 6, 477); Delafontaine had written on the probable compound nature (Comptes Rendus, 1878, 87, 634). Kruss and Nilson, from study of absorption spectrum, maintained composed of nine elements (Chemical News, 1887, 56, 166). See papers by Baskerville for summary of spirited controversy by numerous workers as to this.
1843	TERBIUM.	With erbium in gadolinite.	Mosander.	Ann. Chem. Pharm., 68, 131, 137, &c.	Mosander separated yttria into basic yttria, least basic erbia, and intermediate terbia. Shown by Berlin (1860) to have no existence, although Mosander's results were confirmed by Berzelius ("Lehrbuch," 2nd French edition, 2, 163). Svanberg and Scheerer, Berlin did obtain rose-coloured salts of terbia, since called erbium, but Mosander's yellow erbia, the present terbia, he did not secure (Scand. Naturf. 8 mode Kjöbenhavn, 1860, p. 448).
1843	ERBium.	Gadolinite.	Mosander.	Ann. Chem. Pharm., 68, 131, 137, &c.	(Liebig's Ann., 1866, 137), and Cleve and Högblund (Bull. Soc. Chim., 1872, [2], 18, 193, 289).
1845	<i>Norrium</i> .	Zirconia.	Svanberg.	Oefvers. K. Vet. Akad. Forh., 1845, 34; Pogg. Ann., 65, 317; Ann. Journ. Sci., 21, 1, 257; Belg. Jahreshb., Prakt. Chem., 57 and 97.	Reason for assuming existence, "great variation in atomic weight of oxide." Denied by Berlin (Journ. Prakt. Chem., 58, 145); also Marignac (Comptes Rendus, 50, 952; Chem. Centrbl., 1860, 603). Proved identical with zirconium by Hermann (Journ. Prakt. Chem., 97, 330; Jahreshb., 1866, 189). Taken back by Svanberg, (Journ. Prakt. Chem., 58, 145).
1846	<i>Pelopium</i> .	Bavarian tantalate.	H. Rose.	Pogg. Ann., 60 and 61; Chem. Gaz., 1846, Sept. 5; Am. Journ. Sci., [2], 3, 357.	Discoverer later showed pelopio acid was convertible into columbic and hypocolumbic acids, hence non-existent.
1846	<i>Ilmeium</i> .	Ilmenite.	Hermann.	Journ. Prakt. Chem., 38 and 40; Pogg. Ann., 73	Proved to be columbium.
1850	<i>Aridium</i> .		Ullgren.	Journ. Prakt. Chem., 52; Ann. Chem. Pharm., 76 and 78.	Proved to be composed of iron, chromium, and phosphoric oxides (1854).
1851	<i>Donarium</i> .		Bergmann.	Ann. Ch. Pharm., 80 and 84.	Proved to be thorium (1863).
1852	<i>Thalium</i> .		Owen.	Am. J. Sci., [2], 13, 16, 17.	Two grains white metal like platinum from California gold, with properties unlike those of any known element.
1852	Unnamed.	Gold ores (Calif.).	Genth.	Proc. Acad. Sci. Phil., 9, 209; Am. Journ. Sci., 1853, [2], 15, 446.	Precipitation by potassium ferrocyanide. Specific gravity oxide 5.5 instead of 4.3.
1854	<i>Nameless earth</i> .	Zirconia.	Sjogren.	Journ. Prakt. Chem., 55 and 57.	Setterberg obtained metallic cesium by electrolysis in 1881.
1860	CÆSIUM.	Alkaline salts.	Bunsen and Kirchhoff.	Pogg. Ann., 113, 337; Chem. News, 11, 281.	

1860	Dium.	Finnish tantalate.	Von Kobell.	Ann. Chem. Pharm., 114 and 136; Jour. Prakt. Chem., 83, 193, 449.	Identity questioned by H. Rose, Ste.-Claire Deville, and Hermann. Gives deep blue colour with tin and hydrochloric acid. Marignac and Blomstrand proved it to be columbium (1865). Beketoff prepared rubidium by heating hydroxide with aluminium (1888).
1861	Rubidium.	Lepidolite.	Bunsen and Kirchhoff.	Jahrb., 173; (Chemical News, 3, 357.	Brilliant green line spectrum. Lamy announced same element about same time (Ann. Chem. Phys., 3, 67, 385). Probably same as that discovered by Gentz, as pointed out by Chandler.
1861	Nameless earth.	Calcium group.	Dupré.	Chemical News, 3, 193, 303.	Nickles showed it to contain yttrium, terbium, and didymium (Comptes Rendus, 57, 1740). Delafontaine maintained it to be cerium oxide, while Popp contended it was a mixture of oxides of yttrium, cerium, and didymium (Ann. der Chem. und Pharm., 141, 364, 568).
1861	Thallium.	Selenium residues.	Crookes.	Am. Journ. Sci., 2, 32, 351.	Blue line (hence name) found in spectrum when looking for thallium.
1862	Unnamed.	Native platinum (Oregon). Waste.	C. F. Chandler.	Pogg. Ann., 119, 572; Jour. Prakt. Chem., 91, 316.	Forms characteristic volatile chloride, which is soluble in water precipitated by bases. This dissolves in hydrochloric acid; forming the chloride, which sublimes easily. Not verified.
1862	Wastum.		Bahr.	Journ. Prakt. Chem., 89, 441.	Solubility of double potassium sulphates.
1863	Indium.	Lead, zinc, and arsenic ores.	Reich and Richter.	Pogg. Ann., 122, 646; Am. Journ. Sci., 1865, 2, 38, 420.	Black absorption bands of spectrum. "Still awaiting discovery by more fortunate spectroscopists are the unknown celestial elements, aurium, with a characteristic line at 5597.7, and nebium, having two bright lines at 5007.95 and 4955.03."—Crookes, 1898. See Huggins (Roy. Soc., 1899; Chemical News, 59, 101), with account of observations in 1874.
1864	A new earth.	Calcareous mineral.	Bischoff.	Acta. Univers. Lundensi, 1864. Chemical News, 1869. Nov. Acta. Upsala Sci., 13, 9, 29.	D ₃ line characteristic in this celestial and terrestrial element, doubtless had by Palmieri (1882) from lava, and Hillebrand from uranium minerals. Ramsay secured it and described its properties definitely, however.
1864	Nameless earth.	Zirconia.	Nylander.	"Gases of the Atmosphere," Ramsay.	Absorption bands in spectrum. Solubility chloride in hydrochloric acid.
1866	Nigrium.	Zirconia.	Church.	Proc. R. S., 17, 511; Chem. News, 49, 121, 142, 181; Ber., 1, 146, 193, 337, 382.	Variation in nature of sulphates. Solubility oxide in oxalic acid.
1867	Aurorium.	Aurora.	Angstrom.	Annals N.Y. Lyc. Nat. Hist., 9, 211.	Found by spectroscopy; in very small amounts, but widespread, as shown by Hartley and Ramage. Quite true of most elements (see Gautier on hydrogen and arsenic; Baskerville on Titanium).
(1868)	Nebulium.	Sun's chromosphere, Cleveite.	Janssen, Lockyer, Ramsay.	Comptes Rendus, 81, 493; Chem. News, 34, 159.	Shown by Malet to be a mixture of iridium, rhodium, and iron (Am. Chem. Journ., 1898, 20, 779).
1869	Fargonium.	Zirconia.	Sorby.	Chem. News, 36, 4, 94, 155, 164; and 37, 65.	Separated by difference in solubility of double potassium fluorides.
1869	Nameless earth.	Zirconia.	Loew.	Letter No. 14 in Am. Journ. Sci., 31, 14, 509; Proc. Acad. Nat. Sci. Phila., 29, 194; Comptes Rendus, 87, 148; Chem. News, 38, 100.	Due to insolubility of double potassium sulphate. Marignac proved it identical with terbium (Compt. Rend., 87, 281). Also by Delafontaine (C. R., 87, 606). De Boisbaudran finally demonstrated it to be mixture of didymium, samarium, gadolinium, and terbium (loc. cit., 102, 647).
1875	Gallium.	Gallium.	De Boisbaudran.		
1877	Daryum.	Platinum residues.	Kern.		
1877	Neptunium.	Columbite and ferro-ilimite.	Hermann.		
1877	Mosandrium.	Samaraskite.	J. L. Smith.		

(To be continued).

ELEVENTH ANNUAL REPORT OF
THE COMMITTEE ON ATOMIC WEIGHTS.
DETERMINATIONS PUBLISHED DURING 1903.*

By F. W. CLARKE

DURING the year 1903 comparatively few determinations of atomic weight have been published, but some of the work done is of notable importance. Other work is known to be in progress, and the output for the coming year should be of considerable magnitude. The results which have appeared so far are summarised below.

Potassium and Cæsium.

The memoir by Richards and Archibald (*Proc. Amer. Acad.*, xxxviii., 443; also *Zeit. Anorg. Chem.*, xxxiv., 353) relates primarily to cæsium, but some determinations in regard to potassium were made incidentally. First, potassium chloride, dried at 700°, was precipitated by silver nitrate. The latter had been prepared from a known quantity of pure silver, so that two distinct ratios were determined. Vacuum weights are given throughout, and the reductions were made with $\text{Ag} = 107.930$, and $\text{Cl} = 35.455$; $\text{O} = 16$. For the ratio between KCl and AgCl we have—

Weight KCl .	Weight AgCl .	Atomic weight K .
2.50019	1.80600	39.137
2.50391	1.81325	39.136

For the ratio $\text{Ag} : \text{KCl}$ the data are—

Weight KCl .	Weight Ag .	Atomic weight K .
2.50019	3.61747	39.140
2.50391	3.62284	39.141

Mean of both series. $\text{K} = 39.139$.

Another set of measurements was made by an entirely new method. Potassium nitrate was ignited with weighed quantities of silica; K_2O as silicate remained, and N_2O_5 (or, rather, its decomposition products) was driven off. From the ratio thus ascertained, $\text{K}_2\text{O} : \text{N}_2\text{O}_5$, the atomic weight of potassium was calculated with $\text{O} = 16$ and $\text{N} = 14.040$. The data are as follows:—

Weight KNO_3 .	N_2O_5 lost.	Atomic weight K .
1.81034	0.96694	39.138
3.14564	1.68005	39.142
2.55598	1.36512	39.142

Mean . . . 39.141

For the work on cæsium the material was purified by repeated re-crystallisation of the dichloride, CsCl_2 . By heating this salt to from 90° to 100° in an electric oven it was reduced to CsCl , which was spectroscopically free from other alkaline salts. Several samples of chloride were prepared, and several series of determinations were made, similar to the two sets of chloride analyses given under potassium. The data thus obtained are as follows:—

Ratio $\text{AgCl} : \text{CsCl}$.

Weight CsCl .	Weight AgCl .	Atomic weight Cs .
------------------------	------------------------	-----------------------------

First Series.

3.83054	5.26240	132.901
3.95120	5.36533	132.892
4.22437	5.93555	132.882
3.02935	2.58003	132.901
3.19774	2.72382	132.878

Mean . . . 132.891

Second Series.

2.35068	2.00253	132.858
2.06245	1.75078	132.878
2.56372	2.18358	132.892

Mean . . . 132.876

Third Series.

2.01881	1.71972	132.868
1.77391	1.51093	132.886

Mean . . . 132.877

Fourth Series.

3.08160	2.62484	132.881
3.13117	2.66720	132.872
5.06656	4.31570	132.876

Mean . . . 132.876

Ratio $\text{Ag} : \text{CsCl}$.

Weight CsCl .	Weight Ag .	Atomic weight Cs .
------------------------	----------------------	-----------------------------

First Series.

3.83054	2.45600	132.880
3.95120	2.53351	132.871
2.27237	1.45686	132.891
3.02935	1.94244	132.868
3.19774	2.05023	132.883

Mean . . . 132.878

Second Series.

2.35068	1.50720	132.876
2.06245	1.32251	132.862

Mean . . . 132.869

Third Series.

2.01881	1.29434	132.886
1.77391	1.13743	132.871

Mean . . . 132.878

Fourth Series.

3.08160	1.97590	132.872
3.13117	2.00760	132.879
5.06656	3.24850	132.879

Mean . . . 132.877

The general mean of these eight means gives $\text{Cs} = 132.878$.

By the ignition of calcium nitrate with silica the following data were obtained:—

Weight CsNO_3 .	N_2O_5 lost.	Atomic weight Cs .
3.76112	1.04273	132.882
5.33334	0.92416	132.876
4.81867	1.33590	132.886
5.04807	1.39960	132.871

Mean . . . 132.879

Cæsium bromide was also studied by Richards and Archibald, and two ratios are given by them. First, for the ratio $\text{CsBr} : \text{AgBr}$. $\text{Br} = 79.955$.

Weight CsBr .	Weight AgBr .	Atomic weight Cs .
3.49820	3.08815	132.878
6.20409	5.47673	132.883
7.17300	6.33213	132.880

Mean . . . 132.880

Secondly, for the ratio $\text{CsBr} : \text{Ag}$.

Weight CsBr .	Weight Ag .	Atomic weight Cs .
3.49820	1.77402	132.873
6.20409	3.14606	132.885
7.17300	3.63740	132.884

Mean . . . 132.881

The final values deduced by the authors from all their data are, with $\text{O} = 16$, $\text{K} = 39.140$, $\text{Cs} = 132.879$.

(To be continued.)

* From the *Journal of the American Chemical Society*, xxvi., No. 3.

THE SPECIFIC HEATS OF METALS AND THE RELATION OF SPECIFIC HEAT TO ATOMIC WEIGHT.*

PART III.

By W. A. TILDEN, D.Sc., F.R.S.,

Professor of Chemistry in the Royal College of Science, London

THE object of the experiments of which an account is given in this paper was to determine whether the atomic heats of the elements entering into combination are preserved in the compound at all temperatures, previous results obtained by the author and others having shown that the specific heat of metals of small atomic weight, such as aluminium, increase very rapidly with rise of temperature.

As it is not possible to determine the specific heat of sulphur throughout a long range of temperature, tellurium was chosen for experiment. Compounds of tin, silver, and nickel with tellurium were prepared, and two alloys of silver and aluminium. The specific heats of all these elements were determined at intervals from the boiling-point of liquid oxygen to nearly 500° C. in the case of the less fusible elements, a range of about 680° C. From the mean specific heats the real specific heats at intervals of 100° absolute temperature were calculated, and from the specific heats the atomic heats were deduced. The mean specific heats of the compounds, formed by their union, were also determined, and from these data the molecular heats of the compounds calculated. On comparing the sum of the atomic heats of the elements present with the molecular heat of the compound at the successive temperatures, it was found that there is throughout a very close concordance. The order of difference may be shown by one example:—

Nickel Telluride, NiTe.

Temperature absolute.	Sum of atomic heat of Ni and Te.	Molecular heat of NiTe.
100	9.20	8.38
200	11.08	11.35
300	12.92	12.41
400	13.00	12.92
500	13.49	13.15
600	13.85	13.28
700	14.11	13.35

The results of these experiments show that Neumann's law is approximately true, not only at temperatures from 0° to 100°, but at all temperatures. They also support the view that the specific heat of a solid is determined by the nature of the atoms composing the physical molecules, and is not a measure of the work done in expansion.

The paper concludes with a discussion of the relations of specific heat to atomic weight under different physical conditions—that is, in the solid, liquid, and gaseous states.

potassium thiocyanate, and ammonium thiocyanate were all tried, and the results compared. The first named was useless; of the others, which are all accurate, the thiocyanates gave the best results, and the ammonium salt was better than the potassium. With currents of 0.2 ampère per square decimetre the deposition of 0.05 to 0.08 gm. of gold was complete in five or six hours. With a current of 0.4 to 0.5 ampère, one and a-half to two hours sufficed. The presence of a little persulphate considerably reduced the voltage required. Experiments were also made to determine the best method of removing the deposited gold. Chlorine or bromine water were satisfactory, but slow; aqua regia was risky; the authors recommended a 2 per cent solution of potassium cyanide containing a little hydrogen peroxide, or a persulphate. One or two minutes then sufficed to remove the gold.

An improved form of basin electrode for working with hot solutions was described. A lamp-wick syphon from a small reservoir supplies water to compensate for evaporation.

Mr. CHAS. R. DARLING then read a paper on "Thin-film Electrolysis, and a Proposed Application to Printing," which was illustrated by experiments.

While investigating a process for letter-press printing by electrolysis without the use of ink—an extension of Bain's well-known telegraphic printing—the author found that the final results of electrolysis, when the electrolyte forms only a thin film, often differ materially from those observed in an ordinary cell. In these experiments a carbon or metal plate (it was immaterial which) formed the anode; on this was placed an impression pad, consisting of some sheets of moist blotting-paper; upon this was the trial sheet carrying the electrolyte film, and on this the cathode type or coin. Voltages from 6 to 200 were employed. To obtain a clear image of the type a certain minimum strength of solution is requisite. The first experiments were made with saline solutions; silver nitrate gave a clear permanent black image of the type, but the paper of course darkens on exposure; copper sulphate and nitrate yielded images that faded after a time; the same unexpected result occurred with lead, mercury salts, and bismuth. The best images were obtained with manganese salts. These, consisting as they did of the oxides or hydrates, were quite permanent; all purely metallic deposits, excepting silver, disappeared after a time. In the case of non-saline solutions the paper, which might consist of asbestos or pure Swedish filter-paper soaked in distilled water, acquired the properties of an exposed photographic plate, and on treating with a silver salt and developer, a perfect image of the cathode was obtained, even after a long interval. Reproductions of such "electrographs" are given in the paper. The latent images are not due to hydrogen peroxide, nor to metallic compounds, as they occur with carbon electrodes; but they reside in the surface of the paper in contact with or towards the cathode. The author ascribes them to a class of phenomena that have been investigated by Bose, and termed "the response of inert matter to electrical stimuli," and thinks they are probably the result of some state of strain set up in the film by the current. As regards the fading of the metallic images, this may be simply due to re-combination, although that explanation is not entirely satisfactory.

Dr. H. BORNS asked whether the author had treated his latent images with any solutions before developing.

Mr. N. J. BLUMEN said that in some electrolytic printing that he had carried out they had used some organic solutions with good results.

Mr. FONTANA suggested that the latent images might be due to occluded hydrogen.

Dr. PERKIN thought this supposition could be tested by exposing the paper to an oxidising agent.

Mr. BAWTREE asked whether it were possible to get rid of the latent images. If so, some light would be thrown on their cause.

Mr. PRIDEAUX asked whether the author had tried developing anode images where carbon formed the anode, so that no metal went into solution.

PROCEEDINGS OF SOCIETIES.

THE FARADAY SOCIETY.

Ordinary Meeting, March 21st, 1904.

The meeting was held at the Institution of Electrical Engineers, Dr. O. J. STEINHART in the Chair.

A paper by Dr. F. M. PERKIN and Mr. W. C. PREBBLE on "The Electrolytic Analysis of Gold" was read in abstract by Dr. PERKIN.

The object of the researches described was to arrive at an electrolytic method of estimating gold which should be perfectly accurate and yet far more rapid than the ordinary double cyanide method which the authors, differing from Classen, consider inordinately long, even in hot solutions. Solutions of sodium thiosulphate, cyanide, sodium sulphide,

* Abstract of a Paper read before the Royal Society, March 17, 1904.

Dr. STEINHART did not agree with the "strain" theory put forward by the author. All materials contain some trace of saline matter, and one is almost sure to get chlorine or some such substance given off on electrolysis.

Mr. DARLING, in reply, thanked the speakers for their useful suggestions, many of which he had not had time to follow up, but hoped to in the future. Referring to Mr. Bluman's remarks, organic substances eventually discoloured the paper. He did not think hydrogen the cause of the latent images; certainly, hydrogen peroxide does not destroy the image.

NOTICES OF BOOKS

The Principles of Leather Manufacture. By H. R. PROCTER, F.I.C., F.C.S. London: E. and F. N. Spon, Limited. New York: Spon and Chamberlain. 1903. Pp. 512.

THE present volume is intended not only for the chemist, but also for the practical tanner, though we might well ask why these two capacities should not be combined in one man. Surely, in these days of technical education, there cannot be many "practical tanners" who are not also chemists, while the proper control of the putrefactive and fermentation processes must also involve more than a superficial acquaintance with bacteriology. But whether the reader be one or the other he will doubtless benefit by a study of these pages.

In the twenty-eight chapters into which this book is divided, the author takes us through the history and practice of tanning and leather manufacture from the early primitive methods used by the ancients to the latest processes in vogue, and finally gives us a chapter on waste products and their disposal, including the bacterial purification of sewage. The book is illustrated with over 100 cuts of machinery and apparatus, including a number of microphotographs, these being very interesting. There is also a good index of fourteen pages.

Metallurgical Analysis and Assaying. A Three Years' Course for Students of Schools of Mines. By W. A. MACLEOD, B.A., B.Sc., A.O.S.M. (N. Z.), and CHARLES WALKER, F.C.S. With 109 Figures in the Text. London: Charles Griffin and Company, Limited. 1903. Pp. 318.

ACCORDING to the opinions expressed by the authors, the time necessary to learn metallurgical analysis and assaying is 231 hours in the first year, 495 hours in the second year, and 792 hours in the third. This progressive increase in time seems considerable, but when looked at closely does not amount to many hours per week. For instance, in the third year, which is devoted to assaying and technical analysis, only 24 hours per week for thirty-three weeks is allotted, or four hours a day; this is surely very little. In our student days the metallurgical laboratory was open for eight hours daily, less three lectures per week (of one hour each) for metallurgical students, and we generally had lunch in the laboratory, or, at most, took half-an-hour off for the purpose. However, we will let that pass and come to the methods of instruction proposed.

Naturally, the student commences with chemistry pure and simple, and in Part I. will find instruction in simple qualitative analysis, the preparation and properties of gases, and the group reactions, &c.

Part II. completes the scheme of qualitative analysis, and deals with quantitative analysis by the gravimetric, volumetric, colorimetric, and electrolytic methods.

In Part III., divided into two sections, we come to assaying and technical analysis. Assaying, which may be defined as "the estimation of the commercially important elements in the ores, alloys, or products," is classified into the dry or fire-assay method and the wet way, the latter

including those methods which have been learnt in Part II. The first six chapters in the section on fire-assay methods deal with descriptions of the reagents used, the fitting-up of the assay laboratory, manipulation, the preliminary examination of ores, and introductory experimental work. Then we come to the specific assay of the different metals—tin, lead, gold, silver, copper, sulphur, and mercury; in most cases a separate chapter being devoted to each metal.

The section on Technical Analysis deals with those substances which are connected with metallurgy and metallurgical methods, such as water analysis, the analysis of furnace gases, coal, coke, fire-clays, cements, and slags, and the analysis of iron and steel.

The whole volume is well arranged and written, and although it cannot be claimed that there is anything especially new in the methods described, there is ample evidence of the care with which the compilation has been made, combined with a thorough knowledge of the technical details involved in successfully carrying them out.

We can confidently recommend this book to students, and also to those in practice, who will find it useful for reference. The index is rather scanty, but this may be improved in a future edition.

Elements of Inorganic Chemistry. By HARRY C. JONES. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1903. Pp. 343.

THE author is of the opinion that some of the generalisations of the new physical chemistry can—and ought to be—introduced very early in the study of the science. Chemistry has changed very much in the last twenty years, and we quite agree that some change should be made in the manner of teaching it. He refers in the preface to a typical case, viz., law of electrolytic dissociation, which has been firmly established, by which it is shown that it is the ions and not the atoms that are the active agents chemically. If the student has been taught the contrary in the early stages of his work, he will have to unlearn it later on.

In this volume the physical properties of substances are treated rather more fully than is usual in books for beginners, since the tendency is to bring chemistry and physics closer together.

The book is divided into twenty-seven chapters, the first twelve being of a general character. Chapter XIII. is on the Periodic Law; and, beginning with Chapter XIV., the elements are taken for consideration one by one, and their reactions fully described.

The proofs might have been corrected with more care, as there are not a few misprints. For instance, in the list of elements praseodymium is spelt with an *o* for the *a*, and thallium with one *l*. But this does not detract seriously from the merits of the book, which is well written and arranged. There is a good index covering seventeen pages.

Karl Heumann's Anleitung zum Experimentieren bei Vorlesungen über Anorganische Chemie. ("Karl Heumann's Directions for Lecture Experiments in Inorganic Chemistry"). By Prof. Dr. O. KÜHLING. Braunschweig: Friedrich Vieweg und Sohn. 1904.

THE author of this work died some ten years ago, soon after the appearance of the second edition, and Professor Kühlung, recognising the great value of the work for technical schools and universities, has brought out this third edition. The progress of many branches of inorganic chemistry has necessitated a certain amount of alteration in the text; for instance, space has had to be made for the addition of many important experiments in electro-chemistry, and others performed with the assistance of great extremes of temperature, with liquid air, &c., and this has been done by omitting repetitions of various methods of the preparation of the same compound, or of the preparation of compounds which can be bought very cheaply; these omissions have not at all impaired the usefulness of

the book. The introduction will be found specially valuable in the hints and suggestions it gives to demonstrators and assistants. Much of the information concerning such matters as the handling and use of electrical and lantern apparatus is not to be found in ordinary text-books of practical chemistry, and will be very acceptable. The descriptions of the experiments, though covering only very familiar ground, are conveniently arranged, and perfectly simple and practical. A very short account of the radio-activity of certain substances is interesting and fairly complete; this has been mainly supplied by Prof. Marckwald, and bears the impress of his views; as, for example, in speaking of radio-tellurium as a distinct new substance.

Zeitschrift für Physikalische Chemie. Sechshundvierzigster Band. ("Journal of Physical Chemistry." Vol. XLVI.) Edited by WILH. OSTWALD and J. H. VAN'T HOFF. Leipzig: Wilhelm Engelmann. 1903.

THIS volume of the *Zeitschrift für Physikalische Chemie* is a "Jubiläumband" for Prof. Ostwald in celebration of his jubilee. It contains as frontispiece an excellent portrait of the great chemist, and an introduction by Prof. J. H. van't Hoff, in which a short biographical sketch is given with an appreciation of Ostwald's work as an investigator, thinker, teacher, organiser, and reformer, which is very interesting reading. In so short a space it is not possible to do more than indicate the lines of his activity in these respects, or to make more than passing allusion to the monumental work, the "Lehrbuch der Allgemeinen Chemie," but the author of the sketch certainly does not give the impression of under-estimating the great importance of Ostwald's work in any region. A list of his writings is sufficient to show his extraordinarily great literary activity. The papers contained in the volume come from the pens of Ostwald's pupils from many parts of the world, and relate to different branches of physical chemistry. German, English, and French workers have united to honour the great master, of whom it is not too much to say that mankind owes him an ever-increasing debt.

CORRESPONDENCE.

CATALOGUES GRATIS.

To the Editor of the Chemical News.

SIR,—Taking it for granted that an invitation—prominent in the *CHEMICAL NEWS*, and editorially recommended—was extended to all subscribers, whatever air we might breathe, I wrote for a copy of the book in question, and in due time received the enclosed response, which one might feel disposed to deem amusingly discourteous.

If my correspondent meditated a reservation in disfavour of us Americans, why did he not insert a clause in his advertisement after the style of the old formula "No Irish need apply"? or why not attach a price—say 5, 10, or 15 shillings—with the announcement "Such will be the cost to foreigners"?

That he offered me his Catalogue gratis is his own affair. I applied for it as a book of reference, presuming it to be not unlike the useful "Griffin's Handicraft," for which Griffin, very properly, charged me a few shillings some thirty odd years ago. It was optional with Becker also to set his price.

That Becker would have received no order from me is evident. Home markets supply all our needs. For such is the effect of the high tariff to which he takes exception: it teaches a people to produce whatever they cannot advantageously import. And Americans are not unapt: balances rivalling Becker's are now manufactured in Denver, Colorado, a city which, I doubt not, most people within sound of Bow bells, if they know at all, consider a cowboy's metropolis.

Nevertheless, having publicly offered his Catalogue gratis to the world at large, he should honour all demands. He should murmur with Martial, *ad librum suum*, "I, fuge, sed poteras tutor esse domi," and send his little book freely forth into the unappreciative world.—I am, &c.,

DAVID M. BALCH.

Coronado, San Diego Co., Cal.,
Feb. 22, 1904.

"33-37, Hatton Wall, Hatton Garden,
London, E.C., Jan. 23, 1904.

"DAVID M. BALCH, Esq.,"

"Coronado, San Diego Co., California, U.S.A."

"DEAR SIR,—We have to thank you for your esteemed enquiry for one of our New Chemical Apparatus Catalogues. Although we feel very anxious to oblige you in this matter, we put it to you that we are in a very awkward position, inasmuch as the United States Tariff duty is so high that it is practically impossible for clients in your country to order from England. We have sent hundreds of Catalogues at different times to America, and what is the use of it if no orders result therefrom?—Yours faithfully,

"W. & J. GEORGE, LTD."

AUSTRALIAN PATENT LAW.

To the Editor of the Chemical News.

SIR,—Your readers will probably be interested in hearing that the Governor-General in Council of Australia has decreed, in accordance with the new Federal law, that patent applications for Australia can now be formally made at the Custom House of the capital city of each state. Applications so filed will be marked with the date, hour, and minute of receipt, and the applications will be subsequently recorded at the Patent Office as having been filed at that date. Applications thus filed will not be merely taken in order of their dates, but they will be held to be dated as far as regards novelty from the date of actually filing at the Custom House, unless dated under the convention. Under the convention nearly all the principal countries and colonies have agreed to grant the right to a patentee who has filed an application for a patent in one of the countries or colonies to date any or all the other applications he may make for the same invention in other realms during the year, as of the date of his original first application. The application in Australia can either be a provisional one or a complete. The fees and stamp duties are just double those of an application for Great Britain and Ireland.—We are, &c.,

W. P. THOMPSON & Co.,

Chartered Patent Agents.

6, Lord St., Liverpool.
March 22, 1904.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 9, February 29, 1904.

Cadmium Arsenide.—Albert Granger.—When cadmium is heated in arsenic vapour in presence of hydrogen or another inert gas, the two elements easily combine. The cadmium arsenide is in the form of reddish crystals. Its density at 15° is 6.211, and its composition is Cd_2As_2 . It corresponds to cadmium phosphide, Cd_2P_2 . This arsenide is a much more stable substance than copper arsenide. Its action on acids and the halogens is that of arsenides in general. It is soluble in nitric acid even when diluted with water. It is also attacked by chlorine, bromine, and all chloro-mixtures, as aqua-regia besides, also, oxidising mixtures.

Union of Dinaphthopyrlyl Salts with Di-alcoholic Aromatic Amines.—R. Fosse.—Salts of dinaphthopyrlyl react on the dialcoholic aromatic amines to give new bases, resulting from the substitution of the dinaphthopyrlyl radical for an atom of hydrogen of the cyclic amine :—



The union of the dinaphthopyrlyl radical takes place with the benzenic carbon of the amine in the para-position, according to the formula—



The author establishes, by synthesis, the constitution of one of these products of union. The body resulting from the action of dinaphthopyrlyl bromide on dimethylaniline is identical with the product of condensation of dimethyl-para-aminobenzaldehyde and β -naphthol.

Ethylidene Camphor. Ethylhomocamphoric Acid.—J. Minguin.—The *al*-camphors of the aromatic series, as M. Haller has shown, have a rotatory power considerably higher than the corresponding alcoyl camphors. The author examines ethylidene camphor—the superior homologue of the methylenic derivative—with regard to its rotatory power, and finds that this has also a much greater value than the corresponding *al*-camphor.

Synthesis of $\alpha\alpha$ -Dimethylglutaric and $\alpha\alpha$ -Dimethyladipic Acids.—G. Blanc.—The author easily synthesises $\alpha\alpha$ -dimethylglutaric and $\alpha\alpha$ -dimethyladipic acids by applying the general method of synthesis of the alcohols described by the author and M. Bouveault. The formation of these two acids, starting from the lactones (themselves obtained by the reduction of $\alpha\alpha$ -dimethylsuccinic and $\alpha\alpha$ -dimethylglutaric ethers), prove that the reduction takes place on the carboxyl united to the primary carbon. The author succeeds in generalising this law.

MISCELLANEOUS.

The Paper Trade Directory for 1904.—This edition, edited as usual by "The Doctor," who is the editor of *Paper Making*, includes the names and address of all our Colonial and Indian paper and pulp mills, besides those of Great Britain. Every care has been taken to correct, revise, and bring up to date the information herein given. Three mills have been closed and dismantled during the past year, five have changed hands, and several new paper machines have been put to work in the place of older and smaller machines. We are glad to see that the paper trade is in a fairly prosperous condition.

Ventilation of the House of Commons.—The report of the Select Committee on Ventilation appointed by the House of Commons has been recently issued, and is now reprinted in the form of a pamphlet by Messrs. Hickson, Ward, and Co. It appears from a perusal of this report that the general consensus of opinion condemns mechanical ventilation by means of fans. No matter what precautions are taken, it is impossible to avoid draughts, and even then members of the House complain of tiredness and lassitude in spite of the apparent purity of the air as shown by analysis. It is generally agreed that ventilation can only be achieved successfully by natural means as opposed to mechanical methods.

Percarbonate of Sodium.—S. Tanatar.—The author has already described percarbonate of sodium, $\text{Na}_2\text{CO}_3 + \frac{1}{2}\text{H}_2\text{O}$, obtained by the action of H_2O_2 on a solution of Na_2CO_3 . In aqueous solution this salt gradually decomposes into Na_2CO_3 and H_2O_2 ; thermochemical determinations have shown that the solution of this salt in water is different to a mixture of solutions of Na_2CO_3 and H_2O_2 ; only, as we have not obtained any percarbonates of the heavy metals by the reciprocal action

of Na_2CO_3 and the salts of those metals, we may ask whether the percarbonates are not carbonates in which the H_2O_2 has replaced the water of crystallisation. The discovery of certain compounds ($\text{KF} + \text{H}_2\text{O}_2$; $\text{NaSO}_3 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$), seems to confirm this idea. In an attempt to solve this question, the author has endeavoured to find the coefficient for the division of H_2O_2 between water and ether, then between a solution of Na_2CO_3 and ether; he found that by the addition of Na_2CO_3 , about 30 per cent of the possible quantity of H_2O_2 unites with the salt. Thus percarbonate of sodium in solution is only partially decomposed into Na_2CO_3 and H_2O_2 . Further, many of the salts of the hyperacids behave in this manner. The rise of temperature and the diminution of the concentration increases the hydrolysis. Though these facts may not be sufficient to draw accurate conclusions, the author thinks that percarbonic acid, and the hyperacids in general, contain true higher oxides of the elements.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 952.

A New Method for the Quantitative Separation of Tellurium and Antimony.—A. Gutbier.—I. *Separation by means of Hydrate of Hydrazine.*—The solution should be a hydrochloric one, and free from sulphuric and nitric acids. To the slightly acid solution we add a large excess of tartaric acid and an excess of a dilute solution of hydrate of hydrazine. The tellurium is precipitated; the antimony remains in solution. The latter is boiled with concentrated hydrochloric acid, diluted with warm water, and precipitated with sulphuretted hydrogen. Instead of the hydrate of hydrazine, we might use the hydrochlorate, but not the sulphate. The separation is quite general. The antimony and the tellurium might be precipitated first of all as sulphides, and these subsequently oxidised with nitric acid or aqua regia. II. *Separation by means of Hydrochlorate of Hydroxylamine* (in collaboration with F. Resenschek).—This separation, already suggested by Jannasch and Müller (*Berichte*, vol. xxxi., p. 2338), is effected in a strongly ammoniacal solution. The solution containing the chlorides is treated with a large excess of tartaric acid, and then with 1 or 2 grms. of solid hydrochlorate of hydroxylamine. When the precipitate has settled, it is filtered, and the antimony is estimated in the solution as above. It must first be ascertained that the whole of the tellurium has been precipitated. The two methods give good results, but we do not strongly recommend the precipitation by hydrochlorate of hydroxylamine, on account of the loss of time it occasions.—*Zeit. Anorg. Chem.*, vol. xxxii., p. 260.

INSTRUCTION IN

PURE CULTIVATION OF YEAST. According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations, Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts (brewers', distillers', wine, disease yeasts), moulds, and bacteria.

Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," (London (Spon), 1896). Alfred Jørgensen, "Micro-Organisms and Fermentation," (London and New York (Macmillan and Co.), 1900).

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufacturers, &c.

Further particulars on application to the Director—
ALFRED JØRGENSEN, The Laboratory, Copenhagen, V.

ST. PAUL'S SCHOOL, West Kensington.—An EXAMINATION will be held at the above School on Tuesday, April 12th, 1904, and on the following days, for filling up about Six Vacancies on the Foundation.—Full particulars can be obtained on application to the Bursar.

E. GEORGE & SONS, BOOKSELLERS.

161, WHITECHAPEL ROAD, LONDON, E.

ARE OPEN TO PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English Foreign Learned and Scientific Societies.—Libraries Purchased.
Current Catalogue of General Literature sent on application.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2315.

THE LIQUID STATE.

By P. J. BEVERIDGE, M.A., B.Sc.

WHEN we consider the astonishing resemblance that exists between the nature of gases, as explained by the kinetic theory and the condition of dissolved molecules, the quantitative identity between the gas equation and the equation for osmotic pressure, is it not justifiable to make a tentative application of the kinetic properties of the molecule beyond the case of a mere dilute solute to attempt a general application to the liquid state? The remark is as old as Graham that a solute takes upon itself the liquid character. Is it, then, philosophical to shrink from applying the mechanical properties of the dissolved molecule to the whole of the liquid molecules present, to draw a hard and fast line at dissolved substances, to protest with Pattison Muir that the term molecule can be applied to liquids only in a vague manner and without strict quantitative significance (Watts' Dictionary, Article "Atomic and Molecular Weights"), and not at least to inquire whether the principles which van't Hoff has deduced from osmosis are not applicable to all molecules that are in the liquid condition; in short, to attempt a far reaching generalisation of liquid and gas? It is here intended to inquire whether such an extension of the kinetic theory is possible and congruous with known facts.

The kinetic theory gives us the gas equation, $pV = RT$, expressing *in parvo* the physical properties of a perfect gas. If we are dealing with molecular quantities (1 gram.-mol.) $pV = 84700t$ in mechanical measure, or $pV = 2t$ (more accurately $\times 99$) in thermal measure. From this equation is deduced Avogadro's law, and from it also may be shown that the translatory energy of a gram.-mol. of any gas is $3t$ (or $2 \times 99t$).

Let us then inquire whether provisionally we may consistently assume, first, that the equation $pV = 2t$ can be applied to liquid molecules; secondly, that Avogadro's law holds good in the liquid state; thirdly, that the translatory kinetic energy of the liquid molecule is the same as of the gas molecule at the same temperature; lastly, that the gas molecules in passing into the liquid condition are not greatly, if at all, polymerised. All these assumptions are largely interdependent, and a proof of any one of them goes towards the establishment of the whole.

To consider first of all the question of polymerisation; for unless we have a measure of the molecular weight all further discussion is futile. It is commonly assumed that liquid molecules are very largely polymerised, that in fact they are many times greater than the gas molecules; how many times greater we have no means to judge. On what grounds can we be justified in asserting, on the contrary, that the liquid molecule is practically the same as the molecule of the gas?

In the first place, there is Trouton's law, a numerical statement regarding the heat of vapourisation, which holds good with wonderfully little variation for all liquids. It may be stated thus:—The molecular heat of vapourisation of a liquid boiling at atmospheric pressure, that is the heat required to produce 1 gram.-molecular weight of gas from a liquid at its boiling-point (t° abs.), is equal to about 19t calories ($\pm 2t$ for external work on atmospheric pressure). This law has an accuracy beyond most empirical laws of physics; it is quite comparable in this respect with Dulong and Petit's law, which is so fundamental to the atomic theory. Now, either the liquid molecules are invariable multiples of the gas molecule or they are not. On the one hand, the supposition that the liquid molecule is always just n times the gas molecule (n greater than unity) is hardly conceivable in view of the exceedingly irregular character of molecular polymerisation when it does occur.

On the other hand, suppose we have various liquids whose molecules are respectively made up from, say, two, five, fifty gas molecules, it is simply impossible to suppose that the same amount of heat is required not only to effect the change of physical state but also to dissociate these unequal polymerisations. The only admissible explanation therefore is that liquid molecules are as nearly as possible identical with their gas molecules.

And take the case of acetic acid. Its vapour density indicates a partial polymerisation at boiling-point. But the heat of vapourisation corresponds to the experimental, not to the theoretical molecular weight. Could there be clearer proof that the liquid molecule is polymerised in an equal degree to the gas molecule?

Again, another argument may be deduced from the reduction of the vapour tension of a solvent. The law may be stated thus:—

Vapour pressure of pure solvent =
Decrease of pressure in solution

Total number of molecules, solvent and solute
Number molecules of solute

Or if p, p' be the pressures, N the number of molecules of solvent present in the solution, n the number of molecules of solute—

$$\frac{p}{p - p'} = \frac{N + n}{n}$$

In other words, the decrease of the pressure is proportional to the number of molecules of the volatile solvent which may be supposed exchanged for molecules of non-volatile solute. Given p, p' , and N it is admitted on all hands that we may calculate n the number of molecules of solute, and hence also the molecular weight of the solute. But, conversely, when we are dealing with a known number of molecules of solute and propose to calculate thence N and the molecular weight of the solvent, then at once we receive elaborate cautions on all sides, we are told that the result will not give the molecular weight of the liquid solvent, but the molecular weight of the corresponding gas (Arrhenius, "Text-book of Electro-chemistry," English translation, p. 42). I for my part fail to see how any experiment on a change of condition in the liquid could work out the molecular weight of its gas if the liquid and gas molecules were not identical. And when Arrhenius (*loc. cit.*) triumphantly points out that such an experiment with acetic acid as a solvent will work out to give the mean molecular weight of the partially polymerised acetic acid gas at the temperature of working, one can only reply that there is hardly need of any stronger proof that the gas and liquid molecules are identical.

Polymerisation may indeed be to some extent a characteristic of the change from gas to liquid, but the extent is generally exaggerated. There is strong evidence of polymerisation in the molecules of a solute with increasing concentration, but it will be found that this takes place not so much when the increasing concentration means an approach to the separation or gradual purification of a dissolved liquid, but when approach is being made to the crystallising out of a solid. Thus sulphur in carbon disulphide shows molecular weight as high as S_8 (indeed, I have even reached S_{12}), but if it is a liquid that is in solution, for example, turpentine dissolved in ether, the signs of polymerisation are by no means so conclusive. And even in the case of the solution of solids, the proper way to regard these vapour tension experiments is not to declare that the formula fails for high concentrations, but to admit that even at high concentrations it gives with practical accuracy the average molecular weight of the highly polymerised molecules.

Indeed, if it were not that there seems to be some hazy idea that we are fishing in liquid solutions for the gas-molecular weights of the solutes, the coincidence between the gas-molecular weights of vaporisable substances and their molecular weights in solution would have settled the question long ago.

(To be continued)

THE ELEMENTS: VERIFIED AND UNVERIFIED.

By CHARLES BASKERVILLE, Ph.D., F.C.S., Smith Professor of General Chemistry, University of North Carolina

(Continued from p. 163).

LIST OF PROPOSED CHEMICAL ELEMENTS (continued).

Date.	Name.	Source.	Authority.	Reference.	Remarks.
1877 1878 1878	Lavoesium. "New earths." "X."	Pyrite. Unnamed mineral. Gadolinite.	Prat. Gerland. Soret.	Le Monde Pharmaceutique. Chemical News, 38, 136. Comptes Rendus, 88, 1062.	Identical with holmium subsequently discovered by Cleve, giving bands λ 640 and 5563 with λ 451.5 and 753.
1878	Philippium.	Samaraskite. Samaraskite.	Delafontaine.	Comptes Rendus, 87, 559; Chem. News, 36, 202.	More soluble formate. Characterised by absorption band λ 450 (dysprosium in Soret's "X"). Roscoe (Ber., 1882, 75, 1274), showed it in a mixture of terbia and yttria. Also denied by Crookes (Phil. Trans., 174, 910) and Urbain (Ann. Chim. Phys., 1900, 171, 19, 192).
1878	Decipium.	Samaraskite.	Delafontaine.	Comptes Rendus, 87, 632; Chem. News, 38, 223.	Absorption bands λ 416 and λ 478—one now belonging to samarium of de Boisbaudran—would be decipium now, but Delafontaine said his had no absorption bands.
1878	Ytterbium.	Gadolinite.	Marignac.	Comptes Rendus, 87, 578; Chem. News, 38, 213.	While trying to isolate Delafontaine's philippium.
1879	Scandium.	Gadolinite. Gadolinite.	Nilsen.	Comptes Rendus, 88, 645; Chem. News, 40, 76; Ber., 12, 554; 13, 1439.	Definite spark spectrum (Thalén. Comptes Rendus, 81, 431; 88, 646; Chemical News, 47, 217).
1879	Norwegium.	Gersdorffite.	Pohl	Zeit. d. Geol. Gesell., 31, 480; Comptes Rendus, 89, 47; Chem. News, 40, 25.	Atomic weight ascribed 145.9. Not enough had for work. Mendeleef hoped that it would prove to be eka-cadmium. Brauner suggested $N_g = 219$; not proven.
1879	Samarium.	Samaraskite.	De Boisbaudran.	Comptes Rendus, 88, 322; Chem. News, 40, 99.	Delafontaine's original decipium. Deniaxay separated europium from it.
1879	Barconium.		Wagner's Jahresbericht, Jsb. Chem. Tech., 1879, 8.		Misapprehension.
1879 1879	Thulium. Holmium.	Gadolinite. Gadolinite.	Cleve Cleve.	Comptes Rendus, 89, 478. Comptes Rendus, 89, 478.	In examining Mosander's erbia. Admitted by Cleve to be Soret's "X." Subsequently found by de Boisbaudran to be a mixture of true holmium and dysprosium (Comptes Rendus, 1886, 102, 1003). Crookes says only one of the several bands, 451.5, belongs to dysprosia.
1879	Ouralium.	Russian platinum.	Guyard	Monit. Scient., 53, 9, 795; Chem. News, 40, 57.	Resembles platinum, but softer; atomic weight 187.5. Gives orange melt with potassium cyanide. Unverified. Not to be mistaken for columbium (niobium).
1879	Columbium. Rogorium. Vebium.	Samaraskite. Samaraskite. Lava (Vesuvius).	J. L. Smith. J. L. Smith. Stacchi.	Nature, 21, 146. Chemical News, 41, 116.	
1880 (1886)	Comesium. Ya—GADOLINIUM.	Samaraskite.	Kammerer. Marignac.	Chem. Zeit., 1880, 273. Arch. des Sci. Phys. et Nat., 13, 3, 413; Comptes Rendus, April, 104, No. 16.	These later proved to be complex, but definite elements by the second names had from them. Delafontaine decomposed didymium, which proved to be identical with Yr, Delafontaine's original decipium.
1880 (1885)	Yb—SAMARIUM. Actinium.	Samaraskite. Zinc white.	Marignac. Delafontaine. Phipson.	Chem. News, 44, 73, 138, 191.	Proved to be vanadium oxide. <i>Vida</i> Ramsdellsberg (Ber., 1880, 13, 250).

1882	Di.	Gadolinite.	Cleve.	Chem. News, 15, 273.	Element with ignition spectrum ray \ 4333.5. Found in number of minerals.
1883	Nameless.	Platinum ores.	Wilm.	Berichte, 16, 1498.	
1884	Idiumum.	Vanadium ore.	Websky.	Sitzungsab. Ak. Wiss., Berlin, 66, 661.	
1885	Nioluminum.	Didymium.	Auer.	Monats., 6; Chem. News, 52, 49.	"Meta elements," no doubt of complexity. See work of Kriess, Nilson, Kiewewetter, Brauner, Crookes, Betendorff, Forsberg, Thompson, Dennis, Boudouard, and Baskerville.
1885	Prasodimium.	Didymium.	Auer.	Monats., 6; Chem. News, 52, 49.	
1885	Za.	Didymium.	De Boisbaudran.	Comptes Rendus, 102, 153 and 1887; Chem. News, 53, 63.	Identical with Crookes's Gd. Probably terbium, apparently identical with with Crookes's Gd. See Crookes below.
1885	Zg.	Centre.	Brauner.	Journ. Chem. Soc., 47, 879.	
1886	Zy.	Terbia.	De Boisbaudran.	Comptes Rendus, 152, 103; Chem. News, 53, 63.	Brauner (Monatshefte, 3, 487) didymium β and perhaps didymium γ .
1886	Dysprosium.	Soret's "X" (holmium).	De Boisbaudran.	Comptes Rendus, 102, 1003.	By electric spectrum lines A 5835, 5755, 570, 5679.
1886	Dysprosium X.	Crookes.	Crookes.	Proc. Roy. Soc., 40, 502.	Band A 4515 and A 752.
1886	Unknown.	Crookes.	Crookes.	Proc. Roy. Soc., 40, 502.	Having absorption \ 4515 only. Agreed to by Boisbaudran. (See Holmium).
1886	Austrum.	Orthite.	Linnemann.	Nature, 34, 59; Monatsch., 1886, 773.	Absorption band 550 and 493 not in thulium, erbium, holmium, and dysprosium.
1886	Girvanium.	Argyrodite.	Winkler.	Berichte, 19, 210; Chemical News, 54, 136.	Orthite re-examined by Pribram (Monats., 1900, 21, 148), who confirms de Boisbaudran's assertion (Comptes Rendus, 1886, 102, 1436) that this "austrum" is identical with gallium.
1886	Da.	Didymium.	Crookes.	Chemical News, 54, 13; Nature, 34, 160.	As predicted by Mendeleef.
1886	Sb.	Samarските.			Based upon radiant matter spectroscopy. Strongly opposed by de Boisbaudran (Chemical News, 54, 16). Truly "a nebula of elementary matter," as Petterson put it. See original for vacuum band belonging to each.
	Ga.	Gadolinite.			
	Gy.	Gadolinite.			
	Gz.	Gadolinite.			
	Gx.	Gadolinite.			
	Gy.	Gadolinite.			
1886	Polymestrum.	Glacial debris in Scotland.	Pringle.	Chemical News, 54, 167.	One must read the original to appreciate the properties of these elements, of which we have heard nothing since their announcement. Considering these facts, the country of the discoverer, and the time of the presentation of the paper (during the heat of the Crookes-de Boisbaudran controversy) without inside information, an American might appreciate a joke.
	Nameless (1).				
	Erebodum.				
	Nameless (2).				
	Gadenium.				
	Hesperium.				

(To be continued).

CONTRIBUTIONS TO THE CHEMISTRY OF THE
RARE EARTHS.*

ON LANTHAN-ALUMS—SOME NEW DOUBLE SULPHATES.

By CHAS. BASKERVILLE and EUGENE G. MOSS.

Synopsis.—This paper gives an account of some attempts, not altogether successful, to prepare lanthan-alums. The characteristic properties of lanthanum sulphate, namely, ready formation of a comparatively insoluble hydrate and double salts, appear to interfere. The following new salts, belonging to known types, were prepared:— $\text{La}_2(\text{SO}_4)_3 \cdot \text{Rb}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{La}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{La}_2(\text{SO}_4)_3 \cdot \text{Rb}_2\text{SO}_4$, as well as another model, viz., $3\text{La}_2(\text{SO}_4)_3 \cdot 2\text{Rb}_2\text{SO}_4$ and $3\text{La}_2(\text{SO}_4)_3 \cdot 2\text{Cs}_2\text{SO}_4$.

It may be recalled that lanthanum was one of the elements whose atomic weight was corrected by Mendelëff in the enunciation of the periodic law ("Principles of Chemistry" [English translation], vol. ii., p. 88). Lanthanum is now placed in the aluminum group. Many of the sulphates of elements which form sesquioxides, form the basis of the large class of bodies known as the alums. For these two reasons it is natural to expect lanthanum to form an alum.

Locke (*Am. Chem. Journ.*, xxvii., 281) has called attention to the fact that if an element will form an alum, it does so more readily with cesium sulphate than with any of the other alkaline sulphates. Experiments were therefore begun with lanthanum sulphate and cesium sulphate in an equimolecular mixture. In endeavouring to concentrate the solution to the crystallisation point by heating, either directly or by evaporation upon the water-bath, there resulted almost immediately a precipitation of the nonhydrated lanthanum sulphate, $\text{La}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$. It is well known that lanthanum sulphate dehydrates itself in this manner. We learn also that this body fails to go back into the solution in the same amount of water on cooling. Muthmann and Ritz, in their investigation on the separation of the cerite metals through the solubility of their sulphates, state that the solubility of this nonhydrate varies but slightly with the temperature (*Ber.*, 1898, xxxi., 1723).

As it was impossible to bring about the proper concentration of the mixture by heating, it was placed in a vacuum desiccator and allowed to evaporate under diminished pressure. Beautiful large crystals, symmetrical in form, separated out. The analysis of these crystals, from which the mother-liquor was drained, gave the following percentages:—

	Lanthanum oxide.	Cæsium oxide.
Calculated for—		
$\text{La}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$..	23.85	20.76
$\text{La}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4$..	35.13	30.39
$3\text{La}_2(\text{SO}_4)_3 \cdot 2\text{Cs}_2\text{SO}_4$..	37.57	21.60
Found	33.75	21.72

Another experiment was carried out by placing a similar solution in a freezing-mixture of ice and salt, but no crystals were formed.

During the progress of these experiments, efforts were made to prepare lanthan-potash alum by electrolytic oxidation. Howe and O'Neal prepared iron, cobalt, and chromium alums and attempted to make manganese alums by electrolysis, but without success (*Journ. Am. Chem. Soc.*, 1898, xx., 764). Later Piccini prepared the cesium manganese alum by that method (*Zeit. Anorg. Chem.*, 1899, xx., 12). This method, varied in some respects, was used with lanthanum.

A saturated solution of lanthanum sulphate was prepared by saturating sulphuric acid with lanthanum hydroxide, which had been obtained by precipitation from lanthanum ammonium nitrate. The solution of lanthanum

sulphate was placed within an unglazed porcelain annealing dish. This rested in a large beaker containing more than enough double sulphate of potassium and lanthanum to make a saturated solution. It is difficultly soluble in water, hence the excess of solid. A spiral platinum cathode was placed in the solution in the annealing dish, while a sheet platinum anode rested in the outer liquid. Four Lalande-Edison cells were used, giving a current of about 0.16 ampère, and the process was allowed to continue sixteen hours. No perceptible change in either the outer or inner solution was noted. A few white, opaque crystals separated about the top of the annealing cup. The solution within the annealing cup was taken out and allowed to evaporate spontaneously. In a week's time a mixture of crystals formed. The larger ones were carefully removed by tweezers and analysed.

	Found	Calculated for $\text{La}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$
Lanthanum oxide ..	27.24	27.69
Potassium oxide ..	8.47	8.03

This would indicate the formation of the alum. The amount obtained, 0.1868 grm., was used in the analysis. The remaining smaller crystals and some of the alums gave, on analysis, 47.37 per cent lanthanum oxide. This indicates the coincident formation of the hexahydrate of Frerichs and Smith, which carries 49.17 per cent lanthanum oxide (*Liebigs Ann. Chem.*, cxcl., 460).

In hopes of repeating the above in another experiment with more dilute solutions the current was allowed to run for twenty-three hours. The crystals, a mixture, gave lanthanum oxide, 46.2 per cent, and potassium oxide, 9.71 per cent.

A third experiment was carried out on a larger scale, using 150 c.c. of the double lanthanum potassium sulphate solution and 75 c.c. of the lanthanum sulphate. The current, 0.1 ampère, was allowed to run for forty-eight hours. No crystallisation took place, but four fractions were obtained in the concentration. None of them gave results on analysis worthy of mention.

Similar experiments were carried out with sodium sulphate and the current continued for fifty hours. The solutions obtained were evaporated under reduced pressure. The analysis of the crystals gave:—

	Found.	Calculated for $\text{La}_2(\text{SO}_4)_3 \cdot 2\text{Na}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$.
Lanthanum oxide ..	27.40	27.41
Sodium oxide ..	9.78	10.47

This is doubtless a mixture and its study could not be of interest.

Another experiment with sodium sulphate was carried out with a larger current, 0.4 ampère, and continued for seventy hours. Some pretty needles separated contaminated with fine crystals. It was quite impossible to remove the former and free them from the mother-liquor—they were so soluble. The small crystals on analysis proved to be Cleve's double sulphate (*Ber.*, xi., 912).

	Found.	Calculated for $\text{La}_2(\text{SO}_4)_3 \cdot 2\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$.
Lanthanum oxide ..	36.30	36.04
Sodium oxide ..	13.15	13.87

Experiments were carried out with rubidium sulphate. It may be remarked that it mattered not which one of the alkaline sulphates was used in the mixture; any effort to concentrate by heating always caused a precipitation of the hydrated sulphate, some double salt, or both. In a solution made of rubidium and lanthanum sulphates in theoretical amounts and evaporated in a vacuum desiccator, thin, flat silky crystals formed which, on analysis, gave:—

	Calculated for—	Lanthanum oxide.	Rubidium oxide.
$\text{La}_2(\text{SO}_4)_3 \cdot \text{Rb}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$..	25.77		14.78
$3\text{La}_2(\text{SO}_4)_3 \cdot 2\text{Rb}_2\text{SO}_4$..	43.62		16.77
Found	43.10		17.64

* Presented in abstract at the Cleveland Meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, 1904, xxvi., No. 1.

Lanthanum sulphate is, as remarked, much more soluble in cold than in hot water, the solubility, according to Mosander, being 1 part in 115 of water at 100 and 1 in 6 parts at 13° (*Journ. Prakt. Chem.*, xxx., 380). As one of us (M.) was forced to withdraw from the laboratory, an effort was made in closing up the work to concentrate the rubidium solution at the temperature 45–50° C. The vessel was placed in an air-bath, the temperature regulated, and the evaporation facilitated by drawing a current of dry air over the liquid by means of a suction-pump. Crystals were obtained giving a percentage of 40.4 of lanthanum oxide which would indicate the formation $\text{La}_2(\text{SO}_4)_3 \cdot \text{Rb}_2\text{SO}_4$, where the percentage of lanthanum oxide is 39.13. The body belongs to the type $\text{Di}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4$ (Marignac, *Liebig's Ann. Chem.*, lxxxviii., 242) and $\text{Di}_2(\text{SO}_4)_3 \cdot \text{Ti}_2\text{SO}_4$ (Zschiesche, *Journ. Prakt. Chem.*, cvii., 98).

Efforts were also made to prepare an ammonium alum, but with no more satisfactory results.

Perhaps under more suitable conditions, as spontaneous evaporation at low temperatures, the lanthanum alums may be prepared. Apparently, however, the property possessed by lanthanum sulphate of forming a stable compound with 9 molecules of water with slight elevations of temperature interferes materially with the formation of the alum. Muthmann and Röhl have observed its formation at zero (*loc. cit.*).

Attention has been directed by F. W. Clarke to the alum type—



and the suggestion made that lanthanum, which readily gives $\text{La}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$, forms the model—



These specific properties of lanthanum render the formation of the alum more difficult.

ELEVENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1903.*

By F. W. CLARKE.

(Concluded from p. 164.)

Fluorine.

JULIUS MEYER (*Zeit. Anorg. Chem.*, xxxix., 313) has re-determined the atomic weight of fluorine by a new and simple method. Calcium oxide was converted into fluoride, with suitable precautions, and from the ratio thus measured the atomic weight of fluorine was easily computed. First, the oxide, slaked with water, was converted by hydrochloric acid into chloride. The latter was then repeatedly evaporated with pure hydrofluoric acid, and the resulting fluoride was ignited to constant weight at a red heat. The data, with vacuum weights, are as follows:—

Weight CaO.	Weight CaF ₂ .	Atomic weight F.
6.1883	8.6215	19.036
4.2736	5.9548	19.042
6.2931	8.7658	19.029
5.7767	8.0485	19.038
4.9836	6.9426	19.033

Mean . . . 19.036

Calculated by Meyer with O = 16 and Ca = 40.136.

Iron.

A new determination of the atomic weight of iron, by Baxter (*Proc. Am. Acad.*, xxxix., 245), is based upon the

analysis of ferrous bromide. This salt was sublimed in porcelain tubes, dissolved in acidulated water, oxidised by potassium dichromate, and then mixed with a solution of silver nitrate. The silver bromide was collected on a Gooch filter and weighed. In two experiments the ferrous bromide was also balanced against silver alone. The data, as published, involve a number of corrections, which complicate the table of results. The following corrected weights have kindly been supplied to me by Dr. Baxter. They are reduced to a vacuum, and the calculations represent O = 16, Ag = 107.93, and Br = 79.955.

Weight FeBr ₂ .	Weight AgBr.	Weight Ag.	Atomic weight Fe.
3.55929	6.19873	—	55.856
3.07448	5.35450	—	55.852
2.96102	5.15696	—	55.849
4.00791	6.97983	—	55.862
2.96102	—	2.96234	55.854
4.00791	—	4.00937	55.871
Mean . . .			55.857

One correction still remains to be applied. Ferrous bromide, like the corresponding bromides of cobalt and nickel, when sublimed in porcelain, becomes contaminated with small quantities of sodium bromide. In this case the contamination amounted to 0.138 per cent. Corrected for this impurity the final value for Fe becomes 55.871. This agrees fairly well with the value 55.883 previously determined by Richards and Baxter. The number 55.88 is probably quite nearly correct.

As a check upon the accuracy of this work, Dr. Baxter also re-determined the ratio between silver and bromine. In three independent experiments his data are as follows:—

Weight Ag.	Weight AgBr.	Ratio Ag AgBr.
4.77783	8.31754	57.4428
5.87977	10.23533	57.4459
4.82995	8.40809	57.4441
Mean . . .		57.4443

This is nearly identical with the mean derived from Stas' experiments, viz., 57.4445. From the two experiments of the ferrous bromide series in which both Ag and AgBr were determined, the values for the ratio became 57.444 and 57.442.

Antimony.

The electrolytic method for determining the atomic weight of this element has been investigated by Cohen and Strengers (*Proc. Amsterdam Acad.*, v., II., 543). Antimony and silver were thrown down simultaneously in the same circuit, the former from solutions of trichloride. It was found that the atomic weight thus obtained increased with the concentration of the antimony solution, varying from 120.78 to 121.92, when Ag = 107.93. The concentrations varied from 3.3 to 83.3 grms. of chloride in 100 grms. of solution, and the gain in apparent atomic weight was quite regular. The method therefore involves unknown uncertainties, and is not applicable to the purpose of measuring the atomic weight in question.

Lanthanum.

In the report of this committee for 1902 a set of determinations, by Jones, of the atomic weight of lanthanum was given, and also certain criticisms of the work by Brauner, who claimed that it was vitiated by constant errors. In his reply to Brauner, Jones (*Zeit. Anorg. Chem.*, xxxvi., 92) claims to show that the alleged errors do not exist, and new data are given in corroboration of the former series. In the new work hygroscopic impurity was carefully guarded against, and the lanthanum sulphate was proved to be neutral. Five syntheses of sulphate from oxide, conducted in porcelain crucibles, gave the subjoined results, when O = 16 and S = 32.06.

* From the *Journal of the American Chemical Society*, xxvi., No. 3.

Weight La_2O_3 .	Weight $\text{La}_2(\text{SO}_4)_3$.	Atomic weight La.
1'2161	2'1132	138'79
1'6311	2'8342	138'81
1'7804	3'0938	138'79
1'4168	2'4619	138'80
1'9702	3'4235	138'80
Mean . . .		138'80

The value found in 1902 was $\text{La} = 138'77$.

In these experiments the oxide used was perfectly white. Brauner and Pavlicek heated their oxide, not in porcelain, but in platinum crucibles, and found a higher value for the atomic weight, 139'04. Jones now gives the results of two experiments in platinum, and obtains similar values, as follows:—

Weight La_2O_3 .	Weight $\text{La}_2(\text{SO}_4)_3$.	Atomic weight La.
1'2820	2'2264	139'02
1'3885	2'4110	139'07

In this case the oxide was somewhat discoloured, and most so near the wall of the platinum crucible. Jones regards this as due to a slight oxidation of the material, which would account for the higher atomic weight. The controversy, however, is probably not yet ended. Determinations of atomic weight by some process radically different from either the sulphate or the oxalate method may be necessary to settle the questions at issue.

Cerium.

Upon the atomic weight of cerium two important and elaborate memoirs have appeared; one by Brauner and Batek (*Zeit. Anorg. Chem.*, xxxiv., 103), the other by Brauner alone (*Zeit. Anorg. Chem.*, xxxiv., 207). Only the results of the two investigations can be given here; for details the original publications must be consulted.

First, the salt $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was dehydrated by heating to 440° . The anhydrous sulphate was then reduced by ignition, with suitable precautions, to Ce_2O_3 . In this way, operating upon various fractions of material, Brauner and Batek found:—

Weight sulphate.	Weight oxide.	Atomic weight Ce.
1'5074	0'9130	140'12
1'7079	1'08945	140'32
1'5947	0'90605	140'13
2'6240	1'5805	140'18
1'2161	0'7370	140'38
1'4974	0'9130	140'12
1'2192	0'7386	140'21

Mean . . . 140'21

Calculated with O 16, S 32'06, and reduction to a vacuum.

In the second paper, Brauner gives a series of experiments in which the salt $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was directly reduced to Ce_2O_3 . The data, with vacuum weights throughout, are as follows:—

Weight octahydrate.	Weight oxide	Atomic weight Ce.
1'95890	0'96175	140'26
1'99154	0'96251	140'25
2'31919	1'13027	140'17 (?)
1'95582	0'94679	140'28
1'20961	0'58453	140'21
1'54162	0'74504	140'24
1'67748	0'81074	140'25
2'02739	0'97985	140'26

Mean . . . 140'24

Rejecting the third of these values, in which Brauner suspects a possible loss during the experiment, the mean of the remaining seven becomes 140'25.

For the determinations which the authors carried out by

the oxalate method, the data are too complex for full citation here. Only results can be given. The method involves two steps; first, ignition of cerium oxalate to Ce_2O_3 ; and secondly, determination of Ce_2O_3 in another portion of oxalate by titration with potassium permanganate. From the ratio between Ce_2O_3 and Ce_2O_4 the atomic weight of cerium is calculated. By this process Brauner and Batek made the following eighteen determinations:—

140'28	140'075
140'465	140'075
140'45	140'20
140'165	140'10
140'29	140'32
140'43	140'30
140'38	140'37
140'075	140'42
140'33	140'05

Mean . . . 140'265

One more experiment by this method, cited by Brauner in the second paper, gave $\text{Ce} = 140'246$. As the final result of both investigations, Brauner gives—

$\text{Ce} = 140'25$

This agrees with earlier work by Brauner, and also with determinations by Robinson, and should replace all other measurements of this atomic weight.

Radium.

In the report of this committee for 1902, Madame Curie's determinations of the atomic weight of radium were cited. Her data have since appeared in full, as follows (*Ann. Chim. Phys.*, [7], xxx., 140):—

Weight RaCl_2 .	Weight AgCl .	Atomic weight Ra.
0'09192	0'08890	225'3
0'08936	0'08627	225'8
0'08839	0'08589	224'0

Calculated with $\text{Ag} = 107'8$ (?) and $\text{Cl} = 35'4$. Madame Curie regards the value $\text{Ra} = 225$ as correct to within about one unit. This conclusion finds confirmation in the work of W. Marshall Watts (*Phil. Mag.*, [6], v., 203; and, for Radium, vi., 64), who has studied relations between the spectra of the elements and the squares of their atomic weights. By comparing the spectra of Ba and Ra he finds $\text{Ra} = 225'05$; and for the spectra of Hg and Ra, $\text{Ra} = 224'63$. Mean of all his observations, $\text{Ra} = 224'89$. Runge and Precht, on the other hand, comparing the spectra of Ca, Sr, Ba, and Ra, concluded that the atomic weight of radium is 257'8 (*Physikal. Zeit.*, iv., 285). The apparent instability of radium offers an argument in favour of this higher value. In a later paper Runge (*Phil. Mag.*, [6], vi., 698) criticises Watts's method of calculation, and argues that it is entirely fallacious.

Miscellaneous Notes.

Krypton.—A new determination of the density of krypton, by Ramsay, gives the value 40'81 (*CHEMICAL NEWS*, lxxxvii., 159). The atomic weight therefore is 80'62.

Bismuth.—Adie, seeking to determine the atomic weight of bismuth, obtained discordant results, which were found to be due to small quantities of silica in the material studied (*Proc. Cambridge Phil. Soc.*, xii., 240). To this impurity he ascribes the discrepancies between the measurements of previous observers. A preliminary experiment upon pure bismuth gave $\text{Bi} = 208'8$ approximately.

Tellurium.—The atomic weight of tellurium has been discussed by Koethner (*Zeit. Anorg. Chem.*, xxxiv., 403), by Seubert (*cit. Anorg. Chem.*, xxxv., 205), and by Pellini (*Gazz. Chim. Ital.*, xxxiii., II., 35). Koethner, from an examination of all the published determinations, concludes that the most probable value is $\text{Te} = 126'71$, when $\text{H} = 1$.

Seubert argues in favour of Te = 129.6 or 127.0 with O = 16. Pellini, considering the anomalous position of tellurium in the periodic system, suggests a possible impurity in the form of a radio-active element of higher atomic weight.

Numerical Relations.—This subject is discussed by Mills, under the caption "Numerics of the Elements" (*Phil. Mag.*, [6], v., 543). An attempt is made to compute the atomic weights from a general mathematical formula, and arguments are adduced to show that the most probable value for O is 15.94 when H = 1. Another paper, by Hughes (*CHEMICAL NEWS*, lxxviii., 298), develops relations which suggest that the elements may be constituted analogously to the organic radicals. Still a third paper, by Henry Wilde, also deserves attention (*Mem. Manchester Lit. Phil. Soc.*, xlviii., 1).

International Atomic Weights.—The report of the smaller International Committee for 1903 (*Journ. Am. Chem. Soc.*, 1903, xxv.) has been sharply criticised by Ostwald (*Zeit. Phys. Chem.*, xlii., 637). To this criticism, which related mainly to the standard of values, Seubert published a reply (*Zeit. Anorg. Chem.*, xxxv., 45). The subject of a standard has also been discussed by Winkler (*Chem. Zeit.*, xxvii., 918), whose paper called forth a rejoinder by Landolt and Ostwald (*Ber.*, xxxvi., 3759). In a still later note, Winkler answers his critics (*Ber.*, xxxvi., 4299). For the purposes of this report, these references to literature are sufficient.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, March 10th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. L. F. GUTTMANN, J. H. POLLOK, F. D'O. MEARS, and M. Blood were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harold S. Hammond, Government Laboratory, Kingston, Jamaica; Laurel Cecil F. Oldfield, Lincoln College, Oxford; William D. Page, Constitutional Club, London, W.C.; Thomas L. D. Porter, B.Sc., 161, Downsell Road, Stratford, E.; Louis John E. Riley, Port-of-Spain, Trinidad; Henry Heron Smith, 76, Plumstead Common Road, Plumstead.

Of the following papers, those marked * were read:—

*46. "Mercuric Nitrite and its Decomposition by Heat." By PRAMILLA CHANDI A. RAY.

Mercuric nitrite, hitherto unknown, can be obtained by evaporating *in vacuo* over sulphuric acid, the solution left by decomposing mercuric chloride with silver nitrite. It occurs in groups of light yellow needles which slowly deliquesce and decompose when exposed to the air. The salt and its aqueous solution are stable when sealed up out of contact with air. The solid salt is largely decomposed by water. When heated at about 100° in a vacuum, it melts and intumesces, decomposing for the most part into mercurous nitrate and nitric oxide, but also, to a small extent, into red, crystalline mercuric oxide and the gases of decomposed nitrous anhydride. Mercurous nitrate is also the main product of the decomposition of mercurous nitrite at about 200°, but in this case the nitrate occurs principally as a pseudo-sublimate, derived from the vapours of the decomposing nitrite (*Proc.*, 1903, xix., 78; *Trans.*, 1903, lxxiii., 491).

DISCUSSION.

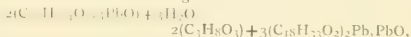
Dr. DIVERS said that, in order to understand the production of mercurous nitrate and nitric oxide from mercuric nitrite, it was necessary (1) to bear in mind that nitric peroxide acts freely on metallic silver to form nitrate and

nitric oxide, and has no action whatever on silver nitrite, and that silver nitrate heated with nitric oxide, even at temperatures well below 200°, interacts with it to form nitrite and nitric peroxide; (2) to assume the same to be true of mercurous nitrite and nitrate; and (3) to refer to the decomposition by heat of mercurous and silver nitrites. Silver nitrite, heated only moderately, behaves almost like mercuric nitrite, except that half the silver is left in the metallic state. But when it is decomposed rapidly, the silver nitrate produced is small in quantity, most of the silver being left in the metallic state and much nitric peroxide escaping. When mercurous nitrite is heated, the ultimate products are also mercurous nitrate and nitric oxide, together with about half of the metal in the free state. But here, visibly, the first products are, for the most part at least, metal and nitric peroxide, which, then, at some distance off, interact to form mercurous nitrate and nitric oxide. It can, therefore, hardly be doubted that the products of decomposition of two molecules of mercuric nitrite by heat are represented by $2\text{Hg} + 4\text{NO}_2$, which then become $(\text{Hg} + \text{O})_2 + 2\text{NO}$, without much loss by vaporisation at the relatively low temperature at which the salt decomposes.

*47. "Note on the Higher Glycerides." By JAMES BALLANTYNE HANNAY.

The higher glycerides, as represented by purified stearin, olive oil, linseed oil, castor oil, cotton-seed oil, rape oil, and earth-nut oil, are all capable of entering into direct combination with lead oxide, the new compounds being formed by heating the oils with excess of finely divided litharge at 170° to 180°, and dissolving out the product with chloroform, petroleum, or carbon tetrachloride. The substance obtained resembles wax, and has no sharp melting-point: it begins to soften at 120°, becomes viscous at 150° to 160°, and is quite limpid at 190°. It commences to boil and decompose at about 280°, the temperature varying a few degrees according to the oil used.

In the case of the olein derivative, the composition may be represented by the formula $\text{C}_{11}\text{H}_{19}\text{O}_2\text{Pb}(\text{C}_{17}\text{H}_{33}\text{O}_2)_2$, where the three atoms of lead are seen to replace six atoms of hydrogen, three in molecules of glycerol, and three in those of oleic acid. This compound probably represents the first step in saponification by lead oxide. The oleic acid derivative, when dissolved in ether, is decomposed by cold water in the following manner:—



glycerol and a basic lead oleate being thereby produced. Lead glyceryl oleate and the corresponding stearate, linoleate, and ricinoleate resemble mercury thymyl acetate in forming a double compound with lead acetate.

The foregoing compounds are stable and not affected by fractional precipitation, neither is the lead displaced by metallic sodium, phosphoric oxide, or sulphur trioxide. The free linkings of the unsaturated glycerides were unaffected by the combination with lead oxide, for the iodine number remained unchanged.

The combination of the lead glyceryl oleate with sulphur chloride is similar to the products obtained from the unsaturated glycerides in general. An examination of the action of sulphur chloride on oils showed that with due precaution the sulphur chloride additive compound was identical in type with the substances obtained by the addition of bromine, iodine, and oxygen. The sulphur chloride saturated the free linking, thus behaving as a bivalent radicle. The oxygen absorption was determined for the same oils, and the results of all these combinations have been tabulated.

During these investigations, no evidence has been obtained of the existence of Hazura's linolenic or *isan*-linolenic acid with six free linkings (with eighteen in the triglyceride); all the iodine numbers are well under the limit for pure linolenic acid with four free linkings, this deficiency being due to the presence of oleic or other acid of a more saturated type.

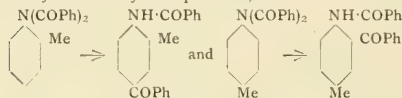
Experiments were made with numerous samples from which the acid had been obtained by three different methods, but only linoleic acid with four linkings was obtained, this result agreeing with that of Reformatzky, who could find no evidence of the existence of acids with six free linkings.

The author showed that Hazura's method of separation with alkaline permanganate has a very variable effect, the oxidation proceeding further than the formation of hydroxy-acids. Hence it is concluded that no acid with an iodine number higher than that corresponding with four free linkings exists in natural oil.

*48. "Isomeric change of Diacylanilides into Acylaminoketones. Transformation of the Dibenzoyltoluidines into the Isomeric Benzoylaminomethylbenzophenones." By FREDERICK DANIEL CHATTAWAY and WILLIAM HENRY LEWIS.

It has been shown recently that acyl groups must be included among those which, under suitable conditions, can pass from the nitrogen of an aromatic amine into the nucleus, displacing a hydrogen atom in a para- or ortho-position relatively to the nitrogen.

An excellent illustration of this intramolecular re-arrangement is furnished by the behaviour of the dibenzoyltoluidines, which at a high temperature under the influence of hydrogen chloride are converted into the isomeric benzoylaminomethylbenzophenones, thus:—



In the transformation of dibenzoyl-o-toluidine, when the acyl group might take up a para- or an ortho-position relatively to the nitrogen, the former is assumed, apparently exclusively. In the transformation of dibenzoyl-p-toluidine, an ortho-position only is available.

As in the case of the analogous transformation of the acylchloroamines, interchange between the *p*-hydrogen atom and the acyl group takes place more readily than that in which the hydrogens in the ortho-positions are concerned.

The yield of 4-amino-5-methylbenzophenone is about 50 per cent, and that of 2-amino-5-methylbenzophenone about 20 per cent calculated on the weight of the corresponding toluidine used.

These hitherto unknown aminoketones were described together with a number of their more important derivatives.

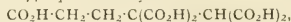
*49. "The Action of Ethyl β -Iodopropionate on Ethyl Disodioethanetetra-carboxylate." By OSWALD SILBERBÄCK. The investigation of the interaction between ethyl β -iodopropionate and ethyl disodioethanetetra-carboxylate has led to the discovery of the following new compounds:—

Ethyl butane- $\alpha\gamma\delta\delta$ -pentacarboxylate, —



boils at 215–218° under 17 m.m. pressure, and yields haloid derivatives which readily give rise to a lactic acid.

Butane- $\alpha\gamma\delta\delta$ -pentacarboxylic acid, —



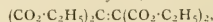
readily loses carbon dioxide, forming butane- $\alpha\gamma\delta$ -tricarboxylic acid, which melts at 122°, and not at 116–120° as previously given (Auvers, Kibner, and Megenburg, *Ber.*, 1891, xxiv., 2895).

Ethyl Δ^2 -dihydrouconate (Δ^2 -butylenedicarboxylate), $\text{CO}_2(\text{C}_2\text{H}_5) \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{C}_2\text{H}_5$, boils at 120–125° under 17 m.m. pressure. The formation of this substance, which constitutes one of the minor fractions, is probably due to the condensation of two molecules of ethyl β -iodopropionate with loss of hydriodic acid.

Hexane- $\alpha\gamma\delta\delta\zeta$ -hexacarboxylic acid was obtained by the saponification of the corresponding ester, which, however,

was not isolated in a pure condition; the constitution of the acid was established by its conversion, with loss of carbon dioxide, into hexane- $\alpha\gamma\delta\zeta$ -tetracarboxylic acid, which latter appears to be identical with Sell and Easterfield's $\alpha\alpha$ -diglutaric acid.

Ethyl ethylenetetracarboxylate, —



is also produced in small quantities, and was identified by conversion into its acid potassium salt. Its formation is probably due to the action of iodine, produced by the decomposition of ethyl β -iodopropionate, on ethyl disodioethanetetra-carboxylate.

*50. "The Heat of Formation of Glucinum Chloride." By JAMES HOLMS POLLOCK.

This research was undertaken in order to obtain the heat of formation of glucinum chloride direct from the metal, for this constant is required in calculating the heats of formation of the other salts of glucinum from the heats of neutralisation of the various acids by the base glucina.

A sample of ground beryl from Limoges was employed in the preparation of pure glucina, and this oxide was converted into the anhydrous chloride by heating with carbon (from cane-sugar) in a current of dry chlorine, the metal being finally obtained from the salt by the action of metallic sodium in a nickel crucible.

On dissolving the metal in hydrochloric acid contained in a calorimeter, it was found that the heat of formation of glucinum chloride in solution was 199.5 calories. The heat of solution of the anhydrous chloride in water is 44.5 calories, and deducting this from the foregoing number, the heat of formation of dry anhydrous glucinum chloride is found to be 155 calories.

*51. "Note on the Composition of Distilled Oil of Limes and a New Sesquiterpene." By HERBERT EDWARD BURGESS and THEODORE HENRY PAGE.

The authors have isolated and identified *l*-terpineol (m. p. 35°) as forming a large proportion of the oxygenated constituents of the oil. The peculiar odour of the oil which is attached to the terpeneol fraction is due to an isomeric liquid terpeneol of slightly lower boiling-point. A new sesquiterpene of partially olefinic nature was also identified, which boils at 131°/9 m.m. and at 262–263° (uncorr.)/756 m.m., in the latter case, with slight decomposition; it has a sp. gr. 0.873 at 15°, and is optically inactive; n_D^{20} is 1.4935 at 15°, and 1.4910 at 19.5°. The sesquiterpene, for which the name "*limene*" is proposed, was characterised by the formation of a trihydrochloride (m. p. 79–80°); this was the only well-defined derivative obtained, and from it the hydrocarbon can be readily regenerated. The same sesquiterpene has been identified in hand-pressed lime oil and lemon oil, and the other oils of this series are being examined for it.

52. "The Nature of a Solution of Iodine in Aqueous Potassium Iodide." By CHARLES HUTCHINS BURGESS and DAVID LEONARD CHAPMAN.

Jakowkin (*Zeit. Physik. Chem.*, 1894, xiii., 529; 1896, xx., 14) has shown that the distribution of iodine between carbon disulphide and an aqueous solution of potassium iodide of varying concentration accords with the assumption of a dissociable compound KI_3 . Dawson's observations (*Trans.*, 1901, lxxix., 238), conducted at a different temperature, confirm this conclusion. The work of the authors has been directed towards the measurement of the

relative velocities of the I^- and I_3^- ions by two independent methods; firstly, by a careful comparison of the iodine carried over to the anode by the same current in cells containing respectively aqueous potassium iodide and a solution of iodine in aqueous potassium iodide, and, secondly, by a comparison of the conductivities of the same solutions.

The mean values of the relative velocities of the I_3^- and I^- ions, determined by the first and second methods, are 0.556 and 0.553 respectively. These practically identical results,

obtained by two different processes, are regarded as confirming the conclusions of previous observers.

A new and symmetrical method of writing the equilibrium equations of the foregoing solution was suggested.

53. "The Reduction of 2:6-Dinitrotoluene with Hydrogen Sulphide." By JULIUS BEREND COHEN and JOSEPH MARSHALL.

In the course of an experiment in which 2:6-dinitrotoluene was reduced with hydrogen sulphide in alcoholic ammonia, a quantity of 2-nitro-4-amino-*m*-cresol was obtained together with 6-nitro-*o*-toluidine. The nitroaminocresol crystallises in dark orange needles, which dissolve readily in dilute acids and alkalis and melt at 190 with decomposition; it forms colourless salts with the mineral acids, and is precipitated from its solution in alkalis by carbon dioxide. On oxidation with lead peroxide and dilute sulphuric acid, it yields 2-nitro-*o*-toluquinone, which crystallises in ruby-red prisms melting at 64–65°, and is converted into 2-nitro-*o*-toluquinol with reduction with sulphur dioxide; the latter crystallises in scarlet needles melting at 117–118°, and dissolving in aqueous alkalis to a violet solution. A solution of bleaching powder in the presence of hydrochloric acid converts nitroaminocresol into chloronitro-*o*-toluquinone, which crystallises in pale yellow, spear-shaped crystals melting at 70–71°. The nitroaminocresol is formed by the incomplete reduction of 2:6-dinitrotoluene to 6-nitro-*o*-tolylhydroxylamine in the same way that trinitrobenzene and trinitrotoluene are converted into the hydroxylamino-compounds (Cohen and Dakin, *Trans.*, 1902, lxxxii., 26). The hydroxylamine derivative, on boiling with dilute hydrochloric acid, changes into the corresponding *p*-aminocresol:—



54. "Acid Esters of Methylsuccinic Acid." By WILLIAM ARTHUR BONE, JOHN JOSEPH SUDBOROUGH, and CHARLES HENRY GRAHAM SPRANKLING.

The methyl hydrogen salts of succinic, *cis*- and *trans*-dimethylsuccinic, and tetramethylsuccinic acids have been obtained by the addition of methyl alcohol to the corresponding anhydrides; they melt respectively at 58°, 38°, 49°, and 63°.

The methyl hydrogen salts of the unsymmetrical monomethylsuccinic, *gem*-dimethylsuccinic, and trimethylsuccinic acids have been prepared by three distinct methods:—(a) from the anhydride, (b) from the neutral ester, and (c) from the acid. The oily products obtained by all three methods from methylsuccinic acid, give practically the same dissociation and esterification of constants.

From *gem*-dimethylsuccinic acid, two distinct acid methyl esters have been obtained; one of these melts at 52° and has a lower dissociation, and also a lower esterification constant than its isomeride, which melts at 40·5°.

The methyl hydrogen salts obtained from trimethylsuccinic acid are oils, the esters obtained from the anhydride and from the acid appear to be identical, but differ from the oil obtained from the neutral ester as regards their dissociation and esterification constants. The results obtained indicate that there is no direct relationship between the two sets of constants.

The esterification constant tends to decrease with an increase in the number of methyl groups present. Walker's generalisation with respect to the dissociation constants does not hold good, as in the succinic series the ratio—

$$\frac{\text{K acid}}{\text{K acid ester}}$$

increases from 2·12 for succinic acid to 27·0 for tetramethylsuccinic acid. The value for *a* in Wegscheider's equation, $\alpha K = K_1 + K_2$, gradually decreases from 0·945 for succinic acid to 0·074 for tetramethylsuccinic acid.

55. "A Note on Phenyltrimethylallylammonium Compounds." By ALFRED WILLIAM HARVEY.

Before the publication of a paper by H. O. Jones (*Trans.*, 1903, lxxxiii., 1400), the author had attempted to resolve phenyltrimethylallylammonium compounds into active constituents. His results, although differing in important details, confirm the conclusions deduced by Barrowcliff and Kipping (*Trans.*, 1903, lxxxiii., 1141) and by Jones (*loc. cit.*).

56. "Estimation of Hydrogen Peroxide in the presence of Potassium Persulphate, by means of Potassium Permanganate." By JOHN ALBERT NEWTON FRIEND.

A correct estimate of the amount of hydrogen peroxide present in a mixture of that substance and potassium persulphate solution is not given under ordinary conditions by titration with potassium permanganate, the values obtained being always too low.

It is found that the proportion of permanganate required to decompose the hydrogen peroxide is subject to the following variations:—(1) It increases with the speed of titration, (2) it varies inversely with the concentration of the persulphate and the volume of the titrated solution, (3) it increases and finally reaches the theoretical amount when the concentration of the sulphuric acid is increased.

A fairly accurate estimation may therefore be obtained if the time of titration is short, and the volume titrated is small, whilst the concentration of the sulphuric acid is fairly great.

57. "A Comparison of the Products of the Hydrolysis of Potato Starch with those obtained from Cereal Starches." By JAMES O'SULLIVAN.

In this investigation, it was established by six series of hydrolytic experiments on potato, Lintner's malt, barley, maize, and rice starches, with both malt-extract and diastase, that the products of the hydrolysis of potato starch, as regards the percentages of maltose and dextrin, bear no quantitative relationship to those yielded by the other starches, and that therefore the products of the hydrolysis of the other starches could not be inferred from the hydrolysis of potato starch.

PHYSICAL SOCIETY.

Ordinary Meeting, March 25th, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A PAPER entitled "Note on the Measurement of Small Inductances and Capacities and on a Standard of Small Inductance" was read by Prof. FLEMING.

The author referred to a paper read before the Society last year by himself and Mr. W. C. Clinton, in which a motor-driven commutator was employed to measure small inductances. It had since been found that very good results could be obtained in the measurement of small inductances by Prof. Anderson's method, by using a telephone in place of a galvanometer and a buzzer in the battery-circuit. The author had found that for long solenoids, at least 50 diameters long, the inductance could be calculated with an accuracy of about 1 per cent by the rule:—Inductance in c.m. = (Length of wire in one unit length of solenoid) × (Total length of wire in the whole solenoid in c.m.). Numerous measurements were given showing the agreement between the measured and predicted inductance of various solenoids and the limits of the dimension-ratio within which the rule was valid. It was also shown that by means of such a predetermined inductance small capacities, such as those of Leyden jars, could be easily measured. A standard of inductance graduated in microhenries suitable for electric resonance experiments and Hertzian wave telegraphy was exhibited. The standard consisted of a spiral of copper wire with special means for producing gradual variation or definite variation in the inductance thrown into a circuit.

Mr. A. CAMPBELL said they had lately measured some self-inductances of the order of 100 microhenries (100,000 c.m.) at the National Physical Laboratory. The method used was practically that of Max Wien as modified by Dolezalek. In the original method two contiguous arms of a Wheatstone's bridge consist of (1) the inductive coil (under test) shunted by a known non-inductive resistance, and (2) an unknown (preferably variable) inductance with an adjustable resistance in series. The other two arms are non-inductive resistances, with a slide-wire between them. The indicating instrument (either an optical telephone or a vibration-galvanometer) is tuned to respond only to a particular frequency, and the source of current is worked at this frequency. Thus, although the source may give a quite irregular wave-form, the instrument practically ignores all but one sine-curve component, and the formula can therefore be easily obtained. The product and the quotient of the inductances in the network are given in terms of non-inductive resistances and p , where $p = 2\pi n$, n being the frequency of the current-source. From these equations the inductances can be separately determined. The modification described by Dolezalek consists in using a current-source giving a nearly pure sinusoidal wave and an ordinary telephone as an indicating instrument. The current-generator is a "microphone hummer." In this a telephone-plate (P) carries a microphone (M). A current from two accumulators is passed through M and the primary of an induction-coil, the secondary being connected with a polarised magnet acting on P. Dolezalek states that, by the use of a "hummer" and a variable inductance standard, inductances of about 0.1 microhenry (100 c.m.) can be readily measured to within 1 or 2 per cent. For obtaining frequencies above 1000 $\sim$ per second, Mr. Campbell has found it desirable to replace the telephone-plate by a steel bar 2.5 c.m. in diameter. In order to make the note in the detecting telephone pure, the latter is tuned by means of a small screw pressing against the ferret-type plate.

Mr. W. DUDELL expressed his interest in the paper, and asked what precautions were taken to ensure that the resistances and connections used were free from self-induction and capacity. He thought that some of the variations in the figures given in Table I. of the paper might be due to these effects.

Dr. FLEMING, in reply, said that in connection with all measurements of small inductances it was essential to continually check the measurements by the aid of a small known inductance made as he described. We were all apt to forget that the ideal "bridges" drawn on paper were not identical with real "bridges," in that the latter had small inductance and capacity in all the arms and connections, and hence formulæ obtained on the assumption that certain branches were absolutely inductanceless and non-capacitous were not strictly correct. In some experiments he had found that great errors were introduced merely by using ordinary flexible twin wires for connections, as these had quite a sensible capacity per metre. In all methods employing the telephone as a detector we were testing the observer quite as much as the method, and not only a perfectly quiet room, but a very acute ear, were necessary if good results were to be obtained. It was becoming important to possess methods of measuring accurately inductances of less than 1 microhenry. The author sketched a plan which he said he had not yet put into practice, but which seemed promising. It involved the use of a Hertz rectangle, and the measurements were made to depend upon the identity in time-period between two conducting paths connecting the same points.

"A Hot-Wire Ammeter for Measuring very small Alternating Currents" was exhibited and described by Prof. FLEMING.

The author said that in alternating-current work, particularly in taking the power-factor of small transformers and of short lengths of cables, the need had been felt for an ammeter not involving the use of iron capable

of measuring currents as small as 0.01 or less of an ampère. He exhibited an ammeter capable of being made to read currents as small as 0.002 with fair accuracy. The arrangement was as follows:—Two very fine platinum or constantin wires, about 1 metre long and 0.05 or even 0.02 m.m. diameter, are supported on a wooden rod with arrangements for adjusting their tensions. These wires are 5 m.m. apart, and are held down at the centre by delicate spiral springs. The two wires are embraced at the middle by a small loop of paper carrying a very small plane mirror. These wires are enclosed in a box, the lid of which carries a lens. By this means the light of a straight carbon filament of a glow-lamp, or of a slit illuminated by an arc-lamp reflected by this small mirror, can be focussed on a screen of ground glass. If a current is passed through one of these wires it sags down slightly, and the square root of the displacement of the image on the screen is almost exactly proportional to the current passing. The instrument can be quickly calibrated by applying a known voltage to the ends of the wire, the resistance having previously been measured corresponding to the range of current used. Examples were given of the use of such an instrument. Suitable very fine wires of pure metals and alloys are now prepared by Messrs. Hartmann & Braun of Frankfurt. These fine wires require "ageing" before use by intermitting a current through them for 12 hours or more.

Mr. W. DUDELL expressed his interest in the paper and said it was difficult to make a satisfactory instrument. The author had said that with a fine constantin wire it was possible to measure currents as small as 2 milliamperes. He asked if this was calculated or observed. There should be a standard method of comparing these instruments, and he suggested using the current necessary to give a deflection equal to one-quarter of the scale distance. Mr. Duddell pointed out that many dynamometers were more sensitive than the instrument shown, and asked the author the order of magnitude of the currents which it was necessary to measure in aerial conductors.

Dr. W. WATSON exhibited and described a form of ammeter for small alternating currents. The current to be measured flows through a piece of iron wire bent into the form of a right angle. This is linked with a similarly shaped piece of nickel wire forming part of a galvanometer circuit. The thermo-E.M.F. at the junction, produced by the heating effect of the current, sends a current through the galvanometer which can be measured in the usual way. The current to be measured is practically proportional to the deflection of the galvanometer.

Mr. A. CAMPBELL described a form of ammeter by Rubens; and Mr. W. A. PRICE referred to an instrument similar to that shown by the author, in which the sag of the wire is measured by the movement of an aluminium pointer.

Dr. FLEMING said he was quite aware that electro-dynamometers had been designed for measuring very small alternating currents, but they were more difficult to make and calibrate than the simple form of hot wire instrument he now exhibited. He had no doubt that the use of a constantin wire of 0.02 m.m. diameter would greatly increase the sensitiveness of the instrument, though he had not actually tried it for want of time. As regards Mr. Duddell's question about the magnitude of the currents flowing into a Wireless Telegraph aerial, that of course depended upon the size of the aerial. In the case of an ordinary 180 foot single aerial the average value was about 0.5 to 1 ampere, but that depended of course on the frequency of the groups of oscillations. The author said that although in the ammeter he exhibited the sag of the working wire was indicated by a mirror, yet he had also used an index-needle, and he had no doubt a good commercial instrument might be made on this plan.

A paper on "Energy of Secondary Rontgen Radiation" was read by Mr. C. G. BARKLA.

To measure the intensity of radiation electroscopes

were placed in a primary beam of Röntgen rays and in a secondary beam proceeding from air in a direction perpendicular to that of propagation of the primary rays. By comparison of the two rates of leak when no absorbing plates were used and when similar aluminium plates were placed before each electroscope, it was found that the absorbability of the secondary rays differed from that of the primary by less than 5 per cent of its value. It was, however, found that a secondary beam of the same intensity as the primary would produce a slightly different number of ions in a given volume of air, consequently the radiations differ slightly in character. The difference in what may be called the "ionising powers" was evidently greater when the primary beam consisted of more penetrating rays. The fraction of energy lost in secondary radiation was very nearly, if not entirely, independent of the character of the primary radiation. The law which the author had previously found to govern the intensity of radiation from gases, was found to be equally applicable to those light solids which are the source of a radiation differing little in character from the primary, *i.e.*, the energy of secondary radiation from these substances situated in a beam of definite intensity is proportional to the quantity of matter through which the primary beam passes. In the passage of X-radiation through air under normal atmospheric conditions, the diminution of intensity due to secondary radiation is of the order of magnitude 0.02 per cent per centimetre. This is a large fraction of the total loss of energy for penetrating rays passing through air. Applying experimental results to J. J. Thomson's calculation of the loss of energy per c.m. due to the passage through a medium containing ions, and considering the electrons as the source of radiation, the number of these per c.c. of air under normal conditions is of the order of 10^{12} . By using the secondary radiation from copper as the primary, approximately the same fraction of the energy was lost in secondary radiation; hence we have quantitative results showing that this radiation from copper, though differing in character from the primary radiation producing it, is of the same nature. Evidence was also found pointing to the conclusion that even from metals which are the source of a secondary radiation differing greatly from the primary, the energy of secondary radiation is of the order of magnitude given by gases and light solids of the same mass.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Notes on the progress of the work of the French Academy of Sciences.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 10, March 7, 1904.

Eurpium.—G. Urbain and H. Lacombe.—The authors find that the magnesium salts of eurpium have nearly the same solubility as those of bismuth, whilst the same salt of gadolinium is considerably more soluble. Hence it is tolerably easy to separate eurpium from gadolinium in the tail of the fractionation. The authors then proceed to calculate the atomic weight of eurpium—(1) By the transformation of the hydrated sulphate into the anhydrous sulphate; (2) by the transformation of the anhydrous sulphate into the oxide; and (3) by the transformation of the hydrated sulphate into the oxide. The results reciprocally check one another, and give almost identical results. The authors therefore conclude that the atomic weight of eurpium is definitely 151.79, and they estimate that this number differs from the real number by less than 0.06.

Action of Carbonic Anhydride on the Ammonium Metals.—Etienne Rengade.—Carbonic anhydride reacts on sodium-ammonium and potassium-ammonium. Below -50° it forms exclusively the alkaline carbonate, with

evolution of hydrogen. At a rather higher temperature an alkaline formate is simultaneously produced, a portion of the hydrogen evolved in the first reaction being thus absorbed. This production of formate by nascent hydrogen and carbonic anhydride in presence of an ammonium metal is analogous to the synthesis effected by M. Moissan by means of the alkaline anhydrides and carbonic anhydride.

General Method of Preparation of Anhydrous Chlorides.—C. Matignon and F. Bourion.—A mixture of chlorine and sulphur chloride constitutes an excellent chlorinating agent for oxides. The reaction must take place at a low temperature, and it allows of the easy preparation of anhydrous chlorides, even in the case of the most exothermic oxides.

Phenylurethanes of Sugar.—L. Maquenne and W. Goodwin.—It is known that phenylisocyanate reacts on polyatomic alcohols belonging to the mannite group, as well as on saccharines, to give insoluble phenylurethanes. The authors apply the same reaction to the reducing sugars and to polyoses without previous hydrolysis. The sugar with a slight excess of carbanil is diluted with two or three times its volume of anhydrous pyridine and then brought to boiling-point. The reaction is rapid, and, after a quick drying process, a crystalline salt separates out. By this method, hitherto unknown phenylurethanes are prepared, as those of the pentoses, hexoses, and certain hydrolysable polyoses, such as lactose, trehalose, and melezitose. Their composition only varies between very narrow limits; however, the analyses are in all cases in perfect accordance with the theoretical composition.

Allyl- and Propenyl-alcohol Ketones.—E. E. Blaise.—The author examines the reaction by which allyl ketones are transformed into propenyl ketones. He finds that the condensation of nitriles with allyl iodide in presence of zinc really gives only the allyl ketone, the propenyl ketone being formed on the elevation of temperature.

Compounds of Saccharose with certain Metallic Salts.—D. Gauthier.—A compound of saccharose with sodium iodide has already been prepared and described. Whilst endeavouring to reproduce this compound by the same method, the author obtained a crystalline product in very distinct prisms. He proves the formula of this substance to be $C_{12}H_{22}O_{11} \cdot NaI \cdot 4H_2O$, differing from that found by Gill. However, this formula is analogous to those proved for compounds of saccharose with potassium iodide and lithium iodide ($-C_{12}H_{22}O_{11} \cdot KI \cdot 2H_2O$; $C_{12}H_{22}O_{11} \cdot LiI \cdot 2H_2O$). The metallic sulphocyanides play parts analogous to those of chlorides, bromides, and iodides, and the author succeeds in obtaining definite products with some of these and saccharose. Ammonium, potassium, and sodium sulphocyanides give beautiful prismatic crystals, whose composition is represented by the formulae $C_{12}H_{22}O_{11} \cdot NH_4CNS \cdot 1\frac{1}{2}H_2O$, $C_{12}H_{22}O_{11} \cdot KCNS \cdot H_2O$, $C_{12}H_{22}O_{11} \cdot NaCNS \cdot H_2O$. Barium sulphocyanide also gives a compound showing prismatic crystals and having the formula $C_{12}H_{22}O_{11} \cdot Ba(CNS)_2 \cdot 2H_2O$.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, April 12, at 5 o'clock, Mr. L. C. Miall delivers the first of three lectures at the Royal Institution on "The Transformations of Animals"; on Thursday, April 14th, at the same hour, Professor Dewar commences a course of three lectures on "Dissociation"; and on Saturday, April 16, at three o'clock, Mr. Cyril Davenport delivers a lecture on "Mezzotints," to be followed on the two succeeding Saturdays by lectures on (1) "Cameos," (2) "Jewellery." The Friday Evening Discourse on April 15 will be delivered by Count Vay De Vaya, on "Korea and the Koreans"; on April 22 by Colonel David Bruce on

"Sleeping Sickness in Uganda"; and on April 29 by Dean Robinson, on "Westminster Abbey in the Early Part of the 17th Century."

Adulterated Drugs and Chemicals.—The United States Department of Agriculture has recently issued a Bulletin, No. 80, on the adulteration of drugs and chemicals. The Bulletin contains three articles; the first is on inferior drugs and insidious methods of deception; the second is on rose geranium oil and its substitutes; and the third on phenacetin, methods of analysis and commercial status. There is a continual cry for cheaper drugs, and in the effort to meet this demand, and at the same time to make a profit, adulteration has spread. This pamphlet will be useful in pointing out the principal methods of adulteration practised, though many tricks, such as colouring with harmless vegetable dyes, are without any danger; still, even in such a case, the fact that the goods are dyed ought to be stated. The article on phenacetin is of some importance; it deals with the history, methods of manufacture, physical and chemical tests, and other points connected with this useful drug. Numerous chemical tests have been proposed for the detection of acetanilid in phenacetin, but so far the ideal method has not been found; among the best of those in use we may mention the bromine test, the saponification test, the mercurous nitrate test, the iodophenol test, and lastly, the isonitrite reaction. Many conflicting statements have been made as to the reliability of the isonitrite test for acetanilid, and though it is at present recognised as an identifying test by the British, German, and United States Pharmacopœias, neither of the two former mentions it in connection with phenacetin, and the latter does not recognise this chemical. We may take it, therefore, that this test has failed.

The Decomposition of Carbonic Oxide in the Blast-furnace.—Rudolf Schenk and P. Zimmermann. The reversible reaction $2CO \rightleftharpoons C + CO_2$ has been the subject of a great many papers. It may be considered from the point of view of the variation of volume, or the variation of pressure which results. The authors have made use of a special apparatus suitable for this purpose, and they have examined the influence of finely divided metals and oxides held in pumice stone. It results, according to them, that the oxides of iron, nickel, and cobalt do not cause any decomposition of the CO, but, on the other hand, the finely divided metals favour it considerably. The examination of the phenomena of the dissociation of CO at different temperatures in the presence of nickel and cobalt, show that the reaction at a high temperature (445°) is bimolecular, $2CO = C + CO_2$, while at a low temperature (310°) it is the result of two reactions:—(1) $CO = C + O$, (2) $CO + O = CO_2$. In the presence of finely divided iron the reaction is more complex.—*Berichte*, vol. xxxvi., p. 1231.

MEETINGS FOR THE WEEK.

- MONDAY, 1st.—Royal Institution, 5. General Monthly Meeting.
—Society of Chemical Industry, 8. "Volatilisation of Lead Oxide from Lead Glazes into the Atmosphere of a China Glaze Sagger and its Effect upon the Leadless Glaze Ware in the same Sagger" and "The Preparation of Lead Glazes of Low Solubility, and some Points to be observed in the Process," by W. A. Thomason. "Addition of certain Solutions upon Aluminium and Zinc," by Watson Smith.
- TUESDAY, 12th.—Royal Institution, 5. "The Transformations of Animals," by Prof. L. C. Miall, F.R.S.
- WEDNESDAY, 13th.—Faraday Society, 8. "Alloys of Copper and Arsenic" by Arthur H. Ewins. "A New Primary Battery" and "Note on Determining Accurately the Percentage of Ozone in Gases not Dissociated by Moderate Heat," by E. G. P. Bousfield.
- Society of Public Analysts, 8. "The Microscopic Examination of Metals" (Illustrated by Lantern Slides), by J. H. B. Jenkins and D. G. Riddick. "Cod Liver Oil and other Fish Oils" and "Note on Mushroom Ketchup," by J. F. Liversidge, F.I.C.

- THURSDAY, 14th.—Royal Institution, 5. "Dissociation," by Prof. Dewar, F.R.S., &c.
- FRIDAY, 15th.—Royal Institution, 9. "Korea and the Koreans," by The Rt. Rev. Monsignor, the Count Vay de Vaya and Luskod, D.P.R.N., &c. J. J.
- SATURDAY, 16th.—Royal Institution, 3. "Mezzotints," by Cyril Davenport, F.S.A.

LONDON HOSPITAL MEDICAL COLLEGE. (UNIVERSITY OF LONDON).

The Summer Session commences on May 2.

The Hospital is the largest in England, nearly 800 beds. In-Patients last year, 13,120; Out-Patients, 182,903; Accidents, 21,879; Major Operations, 2295.

Appointments.—80 Qualified Appointments are made annually, and more than 150 Dressers, Clinical Clerks, &c., are appointed every three months.

Scholarships and Prizes. Enlargement of the Hospital and College, Athletic Ground, Residence, &c.

For particulars of the above, and for Prospectus giving full information as to Course of Study, Fees, &c., apply to—

MUNRO SCOTT, Warden.

Mile End, E.

RADIUM.

FOR SALE—A 5-m.grm. tube of Radium

Bromide of high grade purity and energy. It has been employed in Cancer treatment and other Research Work, and is a guaranteed specimen.—Particulars, "Gamma," Thoru Bank, Leamington in Spa.

ST. PAUL'S SCHOOL, West Kensington.—

AN EXAMINATION will be held at the above School on Tuesday, April 13th, 1904, and on the following days, for filling up about Six Vacancies on the Foundation.—Full particulars can be obtained on application to the Bursar.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC.

As described in the "Report of the Inland Revenue Departmental Committee on Arsenic Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET
LEAD and PIPE, LITHARGE, &c.

INSTRUCTION IN

PURE CULTIVATION OF YEAST.

According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts brewers', distillers', wine, disease yeasts, moulds, and bacteria. Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jørgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufacture, &c.

Further particulars on application to the Director—
ALFRED JØRGENSEN, The Laboratory, Copenhagen, V.

THE CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	4 s.	5 d.
Five lines in column (about 10 words to line)	0	3 6
Each additional line	0	0 6
Whole column	1	15 0
Whole page	3	0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2316.

THE LIQUID STATE.

By P. J. BEVERIDGE, M.A., B.Sc.

(Concluded from p. 169).

We turn next to Avogadro's law. This has long been accepted as having a certain limited and rather indefinite bearing on solution. Nernst, in the preface to his work on Theoretical Chemistry, places it alongside of the doctrine of energy as the most important foundation of all chemical investigations:—"The rule of Avogadro, which seems to be an almost inexhaustible horn of plenty for the molecular theory" (English translation, p. xiii., and *vide* p. 30). And so, on turning to the case of osmotic pressure, whereby the dissolved substance exercises osmotically the same pressure as it would exercise if it were a gas under the influence of Avogadro's law, we find the same qualified acceptance of the law as governing solutes. Well, if we assume this application of Avogadro's law, and if we assume also that the osmotic pressure of the solute is due to the kinetic translatory energy of its molecules within the liquid, then osmotic pressure becomes perfectly intelligible.

For suppose we have the usual apparatus in illustration of osmosis, a porous cell so treated as to make it "semi-permeable," permeable that is to the molecules of solvent, but not to the molecules of solute. Then the molecules of solvent, being free to pass, will produce no effective pressure, while the pressure arising from the motion of the molecules of the solute will be filtered off, so to speak, from all other pressures and attractions. The molecules of the solute will strike against the semi-permeable wall and rebound, they will "bombard" the wall as gas molecules bombard their containing vessel, and if we assume that their translatory kinetic energy is equal to the energy they would have as gas molecules, and also that Avogadro's law holds good with reference to them, then their osmotic pressure will be identical with their calculated gas pressure, and that is experimentally found to be the case.

But everything seems to show that we must go further than this. If solutes are themselves liquids we must apply Avogadro's law to the molecules of the solvent as well. We must apply it to liquids in general. It must be stated that the mean volumes occupied by all the molecules in any particular solution however complicated are the same. We are indeed compelled by thermodynamics to admit that their mean kinetic energy is the same; let us admit that their molecular volume is also the same. Indeed, it does not seem very clear how the one could be true without the other.

Let us see whether this will at all simplify matters. Let us apply it to the law of the diminution of vapour pressure in solutions already quoted. Ostwald points out that no satisfactory explanation has been given of this very simple law. It can be shown by thermodynamics to be a necessary consequence of osmotic pressure, but such thermodynamical reasoning consists in a *reductio ad absurdum* of the opposite proposition, and therefore gives no real explanation at all.

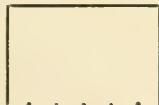


FIG. A.

Let A be the surface of a volatile liquid capable of containing, say, 5 liquid molecules, and enclosed above. A concrete number is taken for simplicity. Within some

certain time t , 5 molecules moving faster than their neighbours will have escaped from the attraction of the liquid, and will take the gaseous form. In another space of time t 5 more will escape, but there will also be rebounds, bringing some of the escaped molecules back into the attraction of the liquid. A point will be reached at length by gradual concentration of the vapour when on an average in the time t 5 molecules leave the liquid and 5 are absorbed by it again. This gives the maximum vapour pressure at the particular temperature. Suppose we denote this pressure by 5.

But now suppose, say, 2 of these molecules of volatile liquid are suddenly replaced by non-volatile molecules, molecules therefore which from whatever reason are unable to leave the liquid. According to Avogadro's law they will fill the same space as those they replace. (They will not necessarily fill the same space as was occupied before, for there have been great pressure changes within the line of surface tension; but they fill the same space as each of the remaining molecules of volatile solvent now fill). See Fig. B. So in the time t there will be 3 molecules escaping

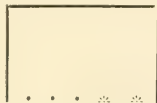


FIG. B.

from the liquid; at first 5 will be absorbed, but as only 3 escape the vapour pressure will be gradually lowered until the point is reached when 3 molecules are striking the liquid in the time t , and 3 escaping; then the pressure will become constant again. Consequently, the pressure which we denoted by 5 will be reduced to a pressure which we must denote by 3. And thus the reduction of the whole pressure is proportional to the number of the molecules exchanged for molecules of non-volatile solute. This is the law already quoted. And so a clear and simple explanation of the law of the reduction of pressure in solution comes in view. Conversely the argument can be used with equal cogency to prove that the molecules occupy the same space in accordance with Avogadro's law.

Further consideration will show that there is here an underlying assumption that the heat required to separate a molecule of vapour from the pure liquid and from the solution is the same; that, in fact, the same kinetic energy of an escaping molecule will enable it to overcome the attraction of the liquid in either case. This is not quite correct, for these heats differ by the heat of dilution of the solution (the heat appearing when a *gram*-molecule of pure solvent is added to the solution); but in dilute solutions this may be neglected.

Yet a further step. We cannot confine our conclusions to the molecules within one liquid. It must be asserted, as a consequence, that the kinetic translatory energy of every molecule of all liquids is the same at the same temperature, and likewise that, given the volume of the *gram*-molecule of any liquid at a certain temperature, we can calculate therefrom what the kinetic pressure must be. The total pressure is a different thing; it is dependent upon inter-molecular attraction.

It may be advisable to note that to hold that the kinetic translatory energy of all liquid molecules at the same temperature is the same and is equal to the gas energy, does not, *prima facie* at least, involve the extension of Avogadro's law. Of the two, the statement with regard to the kinetic energy rests perhaps on surer ground.

Some years ago I was able to come across a remarkable confirmation of this statement. It occurred to me that if we were dealing with liquids of monatomic molecule, so that the whole of their heat energy is translatory and none of it intra-molecular, then, by the solidification of the liquid, the whole of this translatory motion must be still. Thus, if it is true that the energy of this motion is equal to

the gaseous molecular kinetic energy at the same temperature, it follows that it will be equal to $3t$. Now experiments on the vapour pressure of amalgams have shown that metallic molecules are probably monatomic, and this is confirmed by vapour density observations on mercury, cadmium, and zinc. Accordingly, I argued that in liquefying a metallic molecule heat must be supplied equal to $3t$; $3t$ will be the molecular heat of liquefaction. There are disturbing considerations to be taken into account, incipient polymerisation, the changes of volume, &c., but notwithstanding this I found an even closer correspondence to theory than I had expected, and recent determinations of vapourisation heats have brought it closer still. The degree of correspondence with theory is comparable with the results obtained by Ramsay by vapour pressure of amalgams for the molecular weights of the metals, and the delicacy of manipulation renders the accurate determination of these liquefaction heats at high temperatures an exceedingly difficult operation. The law I have already stated as follows:—

The molecular liquefaction heat of a liquid whose molecules are monatomic is equal to the translatory kinetic energy of a gas molecule at the temperature of liquefaction; that is, it is equal to $3t$.

This law I published in the CHEMICAL NEWS in 1897 (vol. lxxvi, p. 264), and attention was again drawn to it by Mr. H. Crompton at last year's meeting of the British Association. I append the table I first used in illustration of the law, amended by the employment of some of Mr. Crompton's heats of liquefaction, which—though he does not give a reference—appear to have been more accurately determined since the first publication of the law. The newer data strengthen the case.

	Melting-point. Abs. t.	Heat of liquefaction (unit mass).		
		A. Calculated.	B. Observed.	Ratio. A : B.
Silver ..	1227°	33·72	26·7	1·27
Cadmium ..	588°	15·52	13·66	1·14
Mercury ..	233	3·45	2·82	1·22
Zinc ..	685°	31·01	28·1	1·10
Platinum ..	2048°	31·24	27·2	1·15
Lead ..	598°	8·67	6·4	1·35
Palladium ..	1773°	49·6	36·2	1·37
Copper ..	1355°	64·2	49·1	1·31
Thallium ..	562°	8·18	7·2	1·14
Aluminium ..	927°	103	80	1·29
Gold ..	1330°	20·2	16·3	1·24
Sodium ..	365°	47·48	32·7	1·45
Potassium ..	335°	25·6	15·7	1·63
Tin ..	503°	12·63	13·62	0·93
Bismuth ..	533°	7·6	12·64	0·603
Gallium ..	286°	12·85	19·11	0·673

The case of tin, bismuth, and gallium is peculiar, but the first two have non-metallic tendencies, and their non-metallic relatives are allotropic. Perhaps sodium and potassium await more accurate determination.

The calculation utterly fails when we come to deal with binary molecules, such as Br_2 , I_2 , and this is itself a corroboration of the law. But one would hardly hesitate to predict that the new gases, argon, krypton, and xenon, will be found to conform with it, unless indeed the close proximity of the solid to the gaseous state in the first two—in the first especially—be found to interfere. Their heats of liquefaction per unit mass would be 6·4, 3·83, 3·12. They may fall 20 per cent below this, but in the case of these permanent gases, as with the most volatile metals, the agreement will probably be much closer. The liquefaction points of the other new gases of the atmosphere are not determined.

Considerations like these open up a wide ground for research. One or two directions may be indicated. We may assume provisionally that in the case of liquids dissolved in volatile liquids the law of variation of vapour pressures is accurately given by the equation quoted, and

refer the divergences noted with increasing concentration to heat of dilution alone, according to the remarks above, and carefully observing these divergences we may collate them with changes in the heat of dilution at varied concentration, and in the surface tension and in the mean molecular volume, all of which must be intimately connected. Again, there is great need for a more extensive and accurate determination of liquefaction heats. And so we may conclude appropriately with the words of Pattison Muir:—"What is wanted now is, therefore, not only further experimental determinations of physical constants of chemically similar compounds, but a great development of the general theory of the structure of matter, especially in the direction of applying this theory to liquid and solid bodies" (Watts' Dictionary, Article "Atomic and Molecular Weights").

SEPARATION OF CHROMIUM AND VANADIUM.

By PAUL NICOLARDOT.

THE separation of chromium and vanadium is very difficult because these elements are found together in considerable quantity, and in almost equal proportions. The separation is almost impossible by the use of ammonium sulphohydrate, and very laborious by the aid of ammonia, as shown by M. Carnot. The method proposed by M. L. Hôte is also not easy of application, and that devised by MM. Matignon and Bourion, in which the action of sulphur is substituted for that of carbon, has the disadvantage of being very complicated.

Separation in the State of Chlorochromic Acid.—It appears to me that the separation of chromium and vanadium would be very simple if the chromium were in the state of chlorochromic acid. It is therefore necessary to treat a mixture of chlorides, chromates, and anhydrous alkaline vanadates with sulphuric acid containing in solution a little anhydride in a very dry bulb. At first the heat evolved is sufficient to start the reaction without artificial heating. The evolution of chromyl chloride is, however, assisted by attaching the apparatus to an air-pump and creating a vacuum, and heating with a spirit-lamp towards the end of the reaction. The last vapours are driven off by a current of dry air. On account of the energy of the reaction a little vanadium is lost mechanically. In order to retain this the bulb should be attached to a little wash-bottle containing a small quantity of strong sulphuric acid. The sulphuric acid used in this reaction should contain a small quantity of anhydride in order to avoid the partial decomposition of the chromyl chloride by the water which is produced during the reaction.

Details of the Experiment.—The compound containing the chromium and the vanadium is melted with a mixture of chlorate and carbonate ($4\text{ClO}_3, \text{CO}_3\text{Na}_2$), or with a large excess of chlorate alone. The small quantities of iron and manganese, if present, are separated by the ordinary methods. The alkaline salts are then concentrated, dried, and melted. The molten mass is completely washed until there is an absence of colour in the wash-water. If there is no iron present, the mixture can be directly melted in the little bulb which was used for the first reaction. Attached to the bulb a little wash-bottle is placed containing a little concentrated sulphuric acid, then a flask containing a dilute solution of soda, through which the gases evolved during the reaction can bubble. The apparatus is attached to a pump.

A current of dry air traverses the apparatus, and a few drops of strong sulphuric acid containing a little anhydride are introduced through a dropping funnel. The reaction at once starts. When it becomes less brisk the pump is brought into play, and a few more drops of acid added, and the air or dry HCl is allowed to enter bubble by bubble. Then the bulb is slightly heated and finally washed until it no longer evolves red vapours. In a very few minutes the whole reaction ceases. The bulb must not be over-

heated, a temperature of 60° being usually sufficient. We prove that all the chromium has been extracted by treating the contents of the bulb on a water-bath, first with SO_3Na_2 , then with excess of ammonia. The precipitate of Cr_2O_3 , if it is abundant, still retains some vanadium, and the process must be repeated. The vanadium can be separated at first if the operation has worked satisfactorily. To estimate it, a little alcohol is added to the liquor. This is heated on a water-bath until all the alcohol is driven off, and then titrated with permanganate. The presence of molybdenum does not interfere with this volumetric estimation.

Separation by means of Condensed Ferric Oxide.—If the compound, which contains vanadium and chromium, also contains a large quantity of iron, the chromium and vanadium can be separated in a still simpler manner. The compound is attacked by hydrochloric acid, the solution then oxidised by nitric acid, or better still by chloric acid, and after this it is evaporated on the water-bath in presence of an excess of hydrochloric acid. I have shown that under these conditions the greater quantity of the acid is driven out (about two-thirds), and a precipitate of condensed ferric oxide is formed which retains the metalloids, the metals remaining in solution.

Chromium sesquioxide, if it contains less than two molecules of water when heated, is always partially transformed into chromic acid. Therefore the chromium in the solution is transformed into chromic acid. It then can be separated, all except the traces which remained in the precipitate of condensed iron oxide; these remaining traces of chromium can be extracted from the ferruginous deposit by treating it with hot water containing some drops of dilute alcohol. After boiling the solution which holds in suspension the precipitate detached from the capsule, ammonium sulphate is added. All the chromium goes into solution, whilst the vanadium remains entirely in the ferric precipitate, from which it can be separated by first washing with ammonia and then fusing with alkaline salts to separate the last traces. The vanadium is then estimated volumetrically.

These two methods can also be used to separate chromium from other metalloids and other metals.—*Comptes Rendus*, March 28, 1904.

THE SEPARATION OF IRON AND CHROMIUM BY MEANS OF FUSED POTASSIUM NITRATE.

By F. SOUTHERDEN, B.Sc., F.I.C.

THE method to be described contains no new principle, depending merely on the oxidation of the chromium by means of KNO_3 and KHSO_4 . The use of fused KHSO_4 in analysis is of ancient origin, though less appreciated for ordinary qualitative work than it deserves to be, and it has long been employed in conjunction with KNO_3 for the estimation of Cr in chrome iron ore. But it does not seem to have been observed before that this fusion and oxidation can be carried out in a few minutes in a test-tube, under proper conditions, without injury to the tube. Apart from ease of manipulation, the substitution of a test-tube for the generally recommended platinum foil or charcoal block may be considered an advantage in dealing with students.

Instead of fusing with KHSO_4 and then adding KNO_3 and raising the temperature as in many operations, the KNO_3 is used as the flux and the KHSO_4 added in small quantity as the decomposing agent. This brings about a much more vigorous oxidation, and gives a more readily fusible "melt."

The precipitate containing the hydroxides of iron and chromium is smeared over a small basin and rotated over the Bunsen flame until approximately dry. It is then scraped into a dry test-tube, one or two smallish crystals of KNO_3 added, and the whole melted by cautiously heating over a low flame. Then a little piece of anhydrous KHSO_4 is dropped in, and the heating continued until brown fumes are copiously evolved. The tube is cooled, water added,

and NH_4OH until alkaline. The fused mass readily dissolves, leaving the iron (and any aluminium) behind as oxide or hydroxide. The residue is filtered off and dissolved in a little concentrated HCl , and tested in the usual way for iron with K_4FeCy_6 . To the filtrate AgNO_3 is added, which gives a red precipitate of Ag_2CrO_4 . A few drops of dilute acetic acid may be necessary to give the chromate indication if any large excess of ammonia is present.

The whole series of operations may be carried out in a few minutes, starting with the wet precipitate. A very insoluble sample of the green oxide of chromium was found to be oxidised almost instantaneously to chromate by this method, and the insoluble violet, CrCl_3 , reacts at once with the fused KNO_3 with out addition of KHSO_4 . Even chrome iron ore is sufficiently decomposed to give a decided indication of chromium in the aqueous extract.

The Technical College, Finsbury.

NOTES ON RAPID SOIL ANALYSIS.

By VINCENT EDWARDS, F.C.S., F.I.C.

ANALYTICAL chemists employed in manure works are often called on to examine and report on soils, also to suggest treatment with fertilisers, an occupation which tends to increase, and one which shows how neglected is this investigation, which should be of supreme importance. Works chemists have difficulties to contend with, they are often short of time, the sample supplied is too small, and so on; in fact, a works chemist bears the same relationship to his official brother as the merchant does to the navy seaman, both doing useful work but under different conditions. Having given some attention to this matter I venture to make some suggestions as to the methods to be employed when the above conditions prevail, as well as a few remarks on the various items.

The preparation of the sample is comparatively simple, breaking up if necessary, and passing through a $\frac{1}{4}$ -inch sieve, which removes stones, the mineralogical character of which should be noted, then grinding in an agate mortar.

Water.—Five grms. is a good quantity to take, drying for five hours in the water-oven. Organic matter and loss on ignition: 5 grms. ignited gently for five hours over an argand lamp, then for half-an-hour over a Bunsen with a rose.

Phosphoric Acid.—10 grms. are gently ignited, evaporated to dryness on water-bath with 20 c.c. HCl , taken up with 10 c.c. more acid, and the insoluble matter filtered off. On cooling, nitric acid solution of ammonium molybdate is added to the filtrate, the beaker allowed to stand forty-eight hours, when the yellow precipitate is collected, washed with small quantities of water till free from acid, dissolved in hot dilute ammonia, the solution evaporated to dryness, and weighed in a platinum dish; the residue contains 3.5 per cent P_2O_5 .

Iron and Alumina.—In this rapid analysis these can be estimated together. The ignited soil is treated with 20 c.c. HCl , evaporated to hard dryness, taken up with hot water and acid, the silicates (insoluble in HCl) dried, ignited, and weighed. The iron and alumina in the filtrate precipitated with ammonia; this repeated so as not to bring down any lime, dried, ignited, and weighed; the P_2O_5 already found being deducted. *Lime.*—Solid ammonium oxalate in powder is added to filtrate, boiled for some time, allowed to stand overnight, and the precipitate collected, then either ignited or the amount found by the volumetric method with permanganate as given in Sutton. *Potash* is best estimated by Tatlock's method, taking 10 grms., treating with 10 c.c. HCl , evaporating to dryness, filtering, evaporating filtrate to dryness, dissolving with hot water and HCl , filtering off any insoluble, evaporating slowly with excess of PtCl_4 ; a very excellent method.

Nitrogen.—A Kjeldahl determination with 10 or even 20

grms.; a special copper flask made by Messrs. Griffin, as suggested by me some years ago, can be used. It may be here pointed out how very necessary a "blank" is; the best H_2SO_4 sometimes contains an appreciable quantity of nitrogen. Nitrates may be looked for by some special colour method.

With regard to the various items:—

Water.—Some text-books say this is of no value. Is this certain? A constant succession of very wet samples of soil show either abnormal rainfall or bad system of drainage. Very wet land will be almost certain to benefit by active manures.

Organic Matter and Loss on Ignition.—There can be no doubt about the importance of a moderate amount of organic matter. If the amount is very low, suggestions might be made as to addition of farmyard manure. In tropical lands a complete exhaustion of the organic matter of the soil is a serious affair, and may make all the difference between a valuable and worthless plantation. Tennant pointed out what a calamity the total loss of vegetable mould was in Ceylon. It is a question if the aid of the Kjeldahl process could not be invoked to estimate rapidly by colour the organic matter in the soil.

Phosphoric Acid.—This determination is of prime importance; nothing can be expected from a soil denuded of this ingredient, as too many are. It is wonderful to think how neglected is this key to the true value of a soil. It is not too much to say that the admirable method suggested by Dr. Dyer, whose important work has justly earned the gratitude of all chemists, at once throws a vivid light on this essential matter. Nitrogen is to some extent supplied by the atmosphere; potash pretty freely present in most soils, even if in rather an inert state; but phosphoric acid, so much depends on the intelligence of the agriculturalist for its sufficient supply. A chemist is asked what percentage of phosphoric acid in the soil calls for treatment. I would say that when under 0.25 per cent on the dry soil enrichers might be applied; under 0.10 per cent the application of suitable phosphatic manure essential. The same figures might also apply to nitrogen and potash; in fact, a scale of valuation of land might be founded on this 0.25 per cent, and be useful to those farmers, auctioneers, &c., who would find a whole figure more satisfactory than decimals.

Iron and Alumina.—A moderate percentage of these soluble in HCl is a decided advantage, and their amount, large or small, give the chemist some assistance in judging as to what form the proposed manure should take if iron is only present in small amount. Dr. Griffiths' experiments as to its beneficial addition as sulphate should be carefully considered.

Lime.—It is needless to say this estimation is of supreme importance; if deficient—that is, under 1 per cent—and the soil fails to effervesce on addition of HCl, basic manure, that is to say, superphosphates with some insoluble or basic slag, or a dressing of lime, should be advised. Many grass lands, ever so much manured, are deficient in lime, and respond well to proper treatment.

Potash.—Artificial supplies may be applied when the figure is under 0.25 per cent. Of course potash is more locked up than phosphoric acid, and there is rightly a tendency to increase the use of potassic fertilisers. The cheapness of kainit, which also supplies magnesia, and so facilitates this, is a move in the right direction.

Silicates (insoluble in HCl).—This figure is of course of interest if excessive, over 90 per cent; it is an indication as to the need of artificial fertilisers.

The following is an example of this "partial" analysis of soil. It was from the garden of an eminent scientific friend in Kent. It may be here stated that the treatment of gardens with artificial manures is generally in a very unsatisfactory state, and it is unfortunate that those who make horticulture a calling do not give more attention to the wants of the soil instead of either totally neglecting the matter, or applying manures in an absurdly haphazard manner.

Partial Analysis of Garden Soil.

	Per cent.
Water	15.95
Dried at 212° F.—	
Organic matter and loss on ignition	2.73
Phosphoric acid	0.08
Iron and alumina	1.94
Lime	0.44
Potash	0.05
Matters not determined	1.13
Silica (insoluble in HCl)	93.63

100.00

Nitrogen, 0.12 per cent

The need of artificial manure is at once apparent here, and the treatment, bearing in mind the object in view, the growth of flowers, is at once indicated. A Peruvian guano, with about 40 per cent of phosphate, 4–5 per cent ammonia, and 3–4 per cent of potash, should have excellent results.

I am quite aware there is not much novelty in the above observations, but the whole matter is so important that a few suggestions may be useful. This is a case where "a little learning" or "a little knowledge" is certainly better than "a great deal of ignorance," and if these simple and inexpensive estimations were more frequently done we should have better agricultural results, and hear less complaints of foreign competition from farmers who have not recognised that some scientific knowledge is essential to success, and by no means replaced by practical skill in agriculture.

Lawes' Works, Barking.

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.*

ATTEMPTS TO PREPARE PRASEODYMIUM AND NEODYMIUM ALUMS—SOME NEW DOUBLE SULPHATES.

By CHARLES BASKERVILLE and HAZEL HOLLAND.

Synopsis.—Pure praseodymium and neodymium sulphates, i.e., free from lanthanum, were prepared and attempts made to form alums by mixing with varying proportions of the alkaline sulphates. The four methods tried, viz., concentration of solutions on the water-bath, in a vacuum desiccator, passing dry cold air over the solution kept at zero, and electrolysis (method of Piccini), failed to give an alum.

The following new double sulphates were prepared:— $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, and $\text{Nd}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, which may serve as types.

The methods of separation of lanthanum and the didymiums were not altogether satisfactory. It was thought, as these bodies are frequently classed together, that perhaps one might form an alum and serve as a method for separating them.

The alums decrease in stability with an increase in the atomic weight of the trivalent metal, while the heavier the univalent metal, the greater the stability. For instance, sodium enters into alums with the lightest of the trivalent metals, as aluminum, vanadium, and chromium. On account of these characteristics and the statement made by Locke (*Am. Chem. Journ.*, xxvii., 281), that "if an alum cannot be formed with caesium, it cannot be formed at all," in most of our experiments caesium was used as the univalent element.

The praseodymium sulphate was prepared from oxide obtained according to the method of Baskerville and Turrentine (*Journ. Am. Chem. Soc.*, xxvi., 46; *CHEMICAL NEWS*, lxxxix., 147). The neodymium sulphate was prepared from the purest neodymium oxide obtained by the

* Presented in abstract at the Cleveland Meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, 1904, xxvi., No. 1.

method of Baskerville and Stevenson (*Journ. Am. Chem. Soc.*, xxvi., 54; *CHEMICAL NEWS*, lxxxix., 151).

No lanthanum was present in either of these preparations, so we hoped to avoid the difficulties encountered in the former paper. In fact, it has been stated that lanthanum might be removed in part from praseodymium and neodymium by heating the sulphates, which will bring about the separation of the lanthanum almost entirely free from the other two bodies. Muthmann and Rölzig made a careful comparative study of the solubility of these sulphates (*Ber.*, xxii., 1720). While both praseodymium and neodymium sulphates are precipitated from concentrated solutions by elevation of temperature, they do not come out so readily as the lanthanum. We did not push the method to such an extent to determine if it would serve as a successful method for the separation finally, but we did learn that it would be very slow.

The praseodymium sulphate was prepared by a solution of the oxide in concentrated sulphuric acid (1:1) in platinum, the excess of acid being evaporated off by heating upon a sand-bath. The pure green crystalline praseodymium sulphate was dissolved in cold water. This standard solution contained for each cubic centimetre 0.05 gm. of the sulphate. The standard solution of caesium sulphate contained 0.039 gm. of sulphate per cubic centimetre. Equivalent amounts of these solutions were mixed and placed in a glass evaporating dish in a vacuum desiccator; within twelve hours pretty green crystals separated out. The liquor was poured off, the crystals dried with alcohol and ether, finally, by pressing between folds of bibulous paper.

The crystals were analysed according to the methods usually employed in the analysis of potash alums, namely, weighed portions were dissolved in cold water, acidified with concentrated hydrochloric acid, the praseodymium hydroxide being precipitated with ammonium hydroxide; the excess was removed by boiling; filtered, washed, and the filtrate evaporated to dryness. Caesium was determined as normal sulphate. A small amount of pure ammonium carbonate was always added after the ammonium salts had been driven off to convert the caesium-hydrogen sulphate into the normal sulphate. The praseodymium hydroxide was ignited in a platinum crucible and heated in the air with a blast-lamp to a constant weight. From a number of determinations and the amount of oxygen yielded by this greenish black residue when it was heated in hydrogen, its formula was taken as Pr_4O_7 .

The first crystals obtained by the method outlined above gave, on analysis, the following:—

	Per cent.
Praseodymium sulphate	61.07
Caesium sulphate	35.57
Water of crystallisation, by difference	3.36
	100.00

The body would therefore have the formula $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ —a new double salt, corresponding to the type $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, similar to Cleve's double lanthanum sulphate and Benedick's $\text{Gd}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (*Zeit. Anorg. Chem.*, xxii., 393), but it is not an alum.

As the relationship of the two sulphates was correct, an attempt was made to increase the content of water of crystallisation by mixing the sulphates at a reduced temperature; zero in the second experiment. When the mixture was kept at that temperature for sixteen hours with a rapid stream of dry air passing over it to facilitate evaporation, very soon exquisite green crystals separated out, which gave on analysis:—

Praseodymium sulphate	58.74
Caesium sulphate	37.64

or virtually the same compound.

The lowering of the temperature failing to raise the percentage of water, the third experiment was carried out at a temperature of 60° C. The beaker was maintained at this temperature by immersion in a carefully regulated

water-bath. The crystals separated out very quickly, and, like the others, possessed the characteristic green colour. The analysis gave—

Praseodymium sulphate	70.08
Caesium sulphate	26.99

While this body also contained 2 molecules of water of crystallisation, the percentage of praseodymium sulphate obtained showed the presence of either a new sulphate or that the crystals analysed constituted a mixture of those previously described and a sulphate probably resembling the nonhydrated lanthanum sulphate.

One experiment was made looking toward the preparation of the praseodymium potassium alum. Theoretical proportions of the sulphates were mixed in a glass evaporating dish and kept in a vacuum desiccator exhausted over night. Green crystals separated out. They were dried and analysed and the compound was found to be a double sulphate containing 4 molecules of water of crystallisation.

Failing to prepare the alum by simply mixing and evaporating the sulphates at different temperatures, Piccini's method of electrolysis was applied to praseodymium and caesium sulphates (*Zeit. Anorg. Chem.*, 1899, xx., 12). A description of the method is given in the previous paper. The experiment was interrupted at the end of forty-eight hours, a few crystals having separated out at the cathode. The solution was decanted and evaporated in a vacuum desiccator. The reduced pressure was continued for several days until sufficient of the crystals were obtained for analysis:—

Praseodymium sulphate	58.14
Caesium sulphate	35.67
Water of crystallisation, by difference	6.19

The compounds, therefore, were double sulphates with 4 molecules of water of crystallisation.

The crystals that separated out at the cathode were analysed with the following result:—

Praseodymium sulphate	56.73
Caesium sulphate	33.63

This is virtually the same double sulphate.

Attempt to prepare Neodymium Alum.

Pure neodymium oxide obtained by the method of Baskerville and Stevenson (*loc. cit.*) was converted into the sulphate in the same manner as described above for praseodymium. Standard solutions of this and caesium sulphate were prepared. Calculated quantities were evaporated *in vacuo*. Beautiful lavender crystals formed, which were analysed according to the same methods as given for praseodymium.

Neodymium sulphate	62.11
Caesium sulphate	32.34
Water of crystallisation, by difference	5.55

The compound was therefore a double caesium neodymium sulphate containing 3 molecules of water of crystallisation, $\text{Nd}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.

Attempts were also made to prepare the potassium neodymium alum by electrolysis. The same method employed in preparing the praseodymium body was used. The crystals which separated out at the cathode gave, on analysis:—

Neodymium sulphate	60.92
Caesium sulphate	33.08
Water of crystallisation, by difference	6.00

This body was also a double sulphate containing 3 molecules of water of crystallisation.

Aluminum salts possess weak basicity, while the praseodymium and neodymium are, comparatively, basic (*Am. Chem. Journ.*, xxvi., 166). This may account in part for our failure to prepare these alums. It is particularly interesting to note in considering these two so-called elements that the one gives a series of double salts with 2 and 4 molecules of water of crystallisation, while the other gives one with 3.

THE ELEMENTS: VERIFIED AND UNVERIFIED.

By CHARLES BASKERVILLE, Ph.D., F.C.S., Smith Professor of General Chemistry, University of North Carolina.

(Continued from p. 171).

LIST OF PROPOSED CHEMICAL ELEMENTS (continued).

Date.	Name.	Source.	Authority.	Reference.	Remarks.
1887	Era. Erß. Tina. Timp. Thulia. Thulia. Samaria. Sma. Soret's X. Xe to X ₁₄ (7). Div to Dik.	Erbia. Erbia. Thulia. Thulia. Samaria. Sma. Soret's X. Didymia.	Krüß and Nilson. Kiesewetter and Krüss.	Ber., 20, 2134; 21, 2310.	Lettered according to source; the Greek characters serve to show each one has one absorption line or band. This is an argument as to the complexity of those elements showing absorption spectra. A most careful study of these and other data offered by Schützenberger, Boudouard, Crookes, Brauner, Muthmann, Dennis, Baskerville, and others enforces the "one band one element" idea of Crookes. Distinctly, however, so far the case is "not proven."
1887	Three unknown new earths.	Didymium from cerite.	Demarcay.	Comptes Rendus, 102, 1552. Comptes Rendus, 104, 580. Comptes Rendus, 102, 1552.	Absorption band λ 475 in didymium spectrum (also Crookes, Comptes Rendus, 102, 1554). Band λ 462 in old didymium spectrum; same giving rise to 475, belong to samarium series according to Crookes (see). Absorption band λ 434 in old didymium spectrum.
1889	Russium.	Thorium from monazite.	Chroustschoff.	Berg, u. Hüt. Zeit., 4, 329; Chem. News, 59, 234.	Measure information as to procedure to be had. Prepared in same manner as Barriere obtained lucium. From many alumina preparations.
1889	Austriacum.	Tellurium.	Brauner.	Trans. Chem. Soc. (Lond.), 407, 411; Monats., 10, 446.	Working on atomic weight of tellurium, Brauner thought he secured homologue atomic weight 214. Later modified claims, stating homologue of argon (Journ. Chem. Soc., 67, 599). See Kothner (Annalen, 1890, 319, 1). Staudenmaier (Zeit. Anorg. Chem., 1895, 10, 180) and Norris, Fay, and Edgerly (Am. Chem. Journ., 1900, 23, 105) concluded tellurium elementary.
1889	Eka-Tellurium.	Tellurium, antimony, and copper.	Grünwald.	Imperial Academy of Sciences, Vienna, 98, 2; Chemical News, 61, 39.	Characteristic unknown element X in 11th series of Mendeleef's table, related to tellurium on one hand and bismuth on other. Probable atomic weight 212 and identical with Brauner's austriacum. Wave-lengths of 16 rays observed in ultra-violet between 2720-2159. See Ames' remarks re Grünwald's helium and coronium conclusions.
1890 1892	Damarium. Gnomium.	Cobalt and nickel.	Much. G. Krüss and F. W. Schmid.	Chem. Zeit., 1890. Berichte, 1889, 22, 11; 22, 1902; 2, 235. Zeit. Anorg. Chem., 1902, 2, 235.	Good fun. Disproved by Winkler (Zeit. Anorg. Chem., 1893, 4, 10).
1892	Masrium.	Egyptian Johnsonite or maserite.	De Boisbaudran.	Chem. Zeitung; Chem. News, 65, 259. Comptes Rendus, 119, 575.	Said to have atomic weight 228, apparently no need to confirm this (Crookes).
1892	Zu.	Samarskite and gadolinite.			Follows samarium spark spectrum; see Europium.
1892	Zc.				(Comptes Rendus, 1469).
1893	Zc.	Terbia.	Hofmann, G. Krüss.	Zeit. Anorg. Chem., 4, 27.	Follows samarium reversion bands. Demarcay's europium.
1894	Probable earth. A new element (?).	French bauxite.	K. I. Bayer.	Chem. Zeit., 18, 671.	Based on some qualitative tests.

1895	Zt.	Terbia.	De Boisbaudran.	Comptes Rendus, 121, 709; Chemical News, 72, 292.	Paper in sealed packet deposited with the French Academy. Beginning of Crookes-de Boisbaudran spirited controversy. Absorption band λ 487.7 does not belong to terbium or dysprosium.
1895	ARGON.	Atmosphere.	Rayleigh and Ramsay.	Roy. Soc. London, January 31, 1895.	Holds its own although numerous efforts have been made to show it to be allotropic nitrogen. Distinctly inert element. A hydrate has been suggested. Also separated by Cavendish (Phil. Trans., 1785, 75, 372; 1788, 78, 271).
1895	Par-Helium.	Helium.	Runge and Paschen.	Math. nat. Mitt., Berlin, 34-3.	Found lines in spectrum could be divided into two sets, and each set consisted of a primary and two secondary series of lines. Later found change of pressure in tube will cause this change—as with oxygen, for example.
1896	Lucium.	Yttria from monazite.	Barriere.	Chemical News, 74, 159, 212.	Shown to be a mixture of yttrium, didymium, erbium, and terbium by Crookes (Chemical News, 71, 259) and Shapleigh (Chemical News, 75, 41).
1896	"Σ" or "Σ-Z."	Gadolinium and samarium.	Demarcay.	Comptes Rendus, 122, 728; 132, 1484.	Extreme fractionation of double magnesium nitrate; atomic weight 151.5. Most characteristic ray, Crookes's anomalous S^2 (fluorescent) and $\frac{1}{2}Z$ of de Boisbaudran (reversion) spectrum (Comptes Rendus, 1901, 132, 148). See Europium.
1895	Unnamed.	Monazite.	Schützenberger and Boudouard.	Comptes Rendus, 121, 273; 122, 697; 123, 782; 136, 1648.	Fractional fusion of nitrates and crystallisation of salts obtained. Atomic weight, 124 (2). Urban states this is mixed with other rare earths. (Bull. Soc. Chim., 31, 19, 48). See Lucium; also Nodden, 88-1d's, "oxide of gadolinium" (Comptes Rendus, 103, 795).
1896	Kosmium, Neokosmium.		Kosmann.	Zeit. f. Elektrochemie, 1896, 7.	Winkler remarks ("Discovery of New Elements, &c.," German Chemical Society, January 11, 1897) —"If it were not for the expense of the patent it might have been thought a pleianity." But see Barriere's Lucium.
1896	Unnamed.	Monazite.	Drossbach.	Berichte, 29, 15; 30, 2452.	Having worked up a large amount of the by-products obtained in extracting thorium from monazite, obtained strongly basic earth, sulphates soluble in double alkaline sulphates. Atomic weight, 100 (2). Boudouard and Schützenberger obtained one with 102. Urban and Budischowsky (Comptes Rendus, 124, 618) fractionated these by acetylacetate compounds in organic solvents into extremes giving values 95 and 112. Mixture. See Lucium.
1897	Metacerium.	Cerium.	Brauner.	Proc. Chem. Soc., No. 101, 69-70; Chemical News, 71.	By fractioning what was thought to be pure ceria, differences in specific gravity, oxides, atomic weight, but no spark-spectral differences. Perhaps has atomic weight 110, according to Brauner.
1897	Glaucodymium.	Didymium.	Chroustschoff.	Journ. Russ. Phys. Chem. Soc., 29, 206.	Distinguished from praseodymium and neodidymium by blue colour of salts. (See these elements; no doubt as to their complexity).
1897	A possible new element.	Cast iron.	Boucher.	Chemical News, 76, 99.	See also Ruddock (Chemical News, 76, 118). Thought to be molybdenum by C. H. Jones (Chemical News, 76, 171). Denied by Boucher.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

ANNUAL GENERAL MEETING, *March 23rd, 1904.*

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

DR. G. BARGER and Dr. S. B. SCHRYVER were appointed scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year. The PRESIDENT then presented the following Report on the state of the Society during the past twelve months:—

Report of the Council.

The Council are in the fortunate position of being able to report that the Society continues to increase and flourish. At the date of the Annual General Meeting last year, the number of Fellows was 2631 (last year this number was incorrectly stated to be 2471); since that date, 170 Fellows have been elected and three reinstated, making a gross total of 2804. Of these, 23 have been removed for non-payment of subscriptions, and the elections of 2 have become void, 28 have resigned, and 17 have died, leaving a net total of 2734 Fellows on our list.

The names of the Fellows who have died are:—H. G. Adshead, J. O. Alexander, A. E. Barrows, Baron de Bush, Samuel Clift, W. H. Corfield, T. H. Dodd, T. W. Fletcher, W. Francis, H. B. Fulton, A. G. Hendry, T. Isherwood, C. James, T. A. Lawson, J. Mactear, J. Reddrop, G. H. Robertson.

As in future Reports the accounts and other statistics of the Society will be given for the calendar year, the following data for the year 1903 may be of interest for purposes of comparison. The number of Fellows on January 1st, 1903, was 2607, and during the year 173 Fellows have been elected and 5 reinstated by the Council, making a gross total of 2785. Of these, the Society has lost 16 by death, 46 from resignations, and 23 by removal for non-payment of subscriptions, giving the number of Fellows in the Society on December 31st, 1903, as 2700.

The Society has to lament the death of a distinguished Foreign Fellow, Professor Wladimir Markownikoff, on February 11th, 1904.

The small number of Fellows elected in the early days of the Society has been further reduced by the death of Dr. William Francis.

The scientific work of the Society during the past session gives evidence of continued activity. Since the last Annual General Meeting, 163 scientific communications have been made to the Society, 107 of which have already been published in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

During 1903, 181 scientific communications were made to the Society, 110 of which were published in the *Transactions* for that year, abstracts of all appearing in the *Proceedings* for 1903.

The *Journal* for 1903 contains also 3882 abstracts, which may be classified as follows:—

PART I.		Pages.	No. of Abstracts.
Organic Chemistry	872	1650	
PART II.			
General and Physical Chemistry		471	
Inorganic Chemistry		443	
Mineralogical Chemistry		119	
Physiological Chemistry		391	
Chemistry of Vegetable Physiology and Agriculture		242	
Analytical Chemistry		566	
	768	2232	
Total in Parts I. and II. ..	1640	3882	

The volume of *Transactions* for 1903 contains 142 memoirs occupying 1490 pages, whilst that for the preceding year contains 160 memoirs occupying 1604 pages.

In April last, Professor Emil Fischer was invited to give the Faraday Lecture in the autumn, and provisional arrangements were made for its delivery early in the present session. Much to the regret of the Council, continued ill-health has prevented Professor Fischer from fulfilling his intention, and for the present the hope of numbering him among the Faraday Lecturers has had to be abandoned. The Council are glad to be able to announce that Professor Ostwald will deliver the Faraday Lecture on Tuesday, April 19th, in the Lecture Theatre of the Royal Institution, kindly lent by the Managers for the occasion.

The Centenary of the Enunciation of the Atomic Theory by Dalton was celebrated by the Literary and Philosophical Society of Manchester in May last, and in company with Sir Henry Roscoe, Professor Thorpe, and Professor Frankland, Vice-Presidents, Dr. Scott, Secretary, and Sir William Ramsay, Foreign Secretary, the President attended the meeting, and presented an address in the name of the Chemical Society.

The triennial award of the Longstaff Medal to the Fellow of the Society who, in the opinion of the Council, has done the most to promote chemical science by research in the interval since the last presentation, was made, on the recommendation of the Research Fund Committee, to Professor W. J. Pope, F.R.S., for his researches on the stereochemistry of compounds of elements other than carbon.

The Fifth International Congress of Applied Chemistry was held in Berlin in June last, and the President attended as the representative of the Society. An invitation to the Congress to hold its next meeting in London, given by the President of the Society of Chemical Industry, was supported by the President, but on a vote being taken Rome was chosen as the place of the meeting in 1905.

The Council welcomed the opportunity of sending a letter of congratulation to their distinguished Foreign Fellow, Professor Mendeleeff, on the occasion of his seventieth birthday, which occurred on February 9th last.

The increase in the use of the Library mentioned in last year's report has been maintained, as 975 books were borrowed from the Library, as against 925 during the previous year. The additions to the Library comprise 115 books, of which 49 were presented, 268 volumes of periodicals, and 48 pamphlets; as against 84 books, 338 volumes of periodicals, and 23 pamphlets last year. The corresponding numbers for the year ending December 31st, 1903, are 991 books borrowed, the additions to the Library being 126 books, of which 51 were presented, 271 volumes of periodicals, and 43 pamphlets.

The changes proposed in last year's report with regard to the Library have now been carried out, and cases have been erected in one of the rooms in the basement for the storage of the less used books. These cases will accommodate about 3500 volumes, and so provide room for the growth of the Library for about seven years. An equal number of cases can be added at any future period without cost beyond that of the cases themselves.

Mr. F. W. Clifford was appointed Librarian on July 1st. The Council regret to have to record the death, on May 10th, of Mr. Josiah Hall, who for twenty-five years had been Collector to the Society, and who retired in 1895 with a pension of £130 a year. It was decided to grant to Mrs. Hall, his widow, an annuity of £30.

The Society has been the fortunate recipient of two handsome busts in bronze of distinguished chemists, that of Liebig (a copy of the one in Munich) having been presented by Dr. Messel, and that of Dalton, which has been modelled from all available sources by Miss Levick, by Professor Thorpe. Two interesting photographs of portraits have also been received, one of Roger Bacon, presented by Mr. Oscar Guttman, and one of Dr. Wm. Prout, F.R.S., from his son, the Rev. T. J. Prout.

At an Extraordinary General Meeting of the Society held

on July 2nd, the proposal of the Council to alter By-law I. so that the annual publications of the Society should not be sent to Fellows who are in arrear with their subscriptions, was unanimously approved. To give effect to this change in the By-law, the *Journal* is now issued to Fellows on the last day instead of the first day of the month. An extra number of the *Transactions* was issued on December 31st to provide for the publication of papers which would have appeared on January 1st, 1904, under the old arrangement, and now that the change has been made the net result is that Fellows receive the monthly parts of the *Journal* a day earlier than heretofore.

The first part (Authors' Index) of the Collective Index for the decade 1893-1902, promised provisionally for 1904, was issued in January to those Fellows who had made application for it in accordance with the printed notices circulated with the monthly parts of the *Journal* since last July, and it is hoped that the subject index for the same period may be ready before the end of next year. The rapid publication of the Authors' Index is due to the untiring energy and devotion of the Indexer, Mrs. Dougal, and has in no way interfered with the issue of the Annual Index at the end of February, which has been customary since she undertook the work involved in its preparation.

The Second Report of the Joint International Committee on Atomic Weights, which now includes Professor Moissan as the representative of France, with its revised table of atomic weights, has been issued to Fellows both in the *Proceedings* and in the *Journal*.

The Council resolved that the rooms of the Society should be closed not later than 10.30 p.m. on those evenings on which meetings are held, and, as very few Fellows were found to use the Library on Saturday afternoons, it was further resolved that it should be closed at 2 p.m. on Saturdays from the beginning of the present year.

Grants amounting in all to £232 have been made during the year from the Research Fund, of which amount £15 has been returned.

The Council desires to record its deep sense of obligation to Dr. Horace T. Brown for the ability and patience with which he has discharged the duties of Treasurer during the past year. Finding on taking office that a complete re-organisation of the method of collecting the contributions of Fellows and of keeping the Accounts of the Society was immediately necessary, he did not shrink from the immense labour involved in establishing a new system and getting it into operation. The nature of the changes which have been made is explained below, and it is obvious that great sacrifices of time and of personal effort were involved in the process. It is therefore with the utmost regret that the Council has received from Dr. Brown an intimation that his engagements no longer permit him to retain office.

Hitherto, it has been customary for the Treasurer to close the Books of the Society a few days before the Annual General Meeting, and to make up the Accounts to a date as near to that of the Annual Meeting as possible. This arrangement has given rise to considerable inconvenience, owing, in the first place, to the short time allowed to complete the financial statements, and, secondly, to the impossibility of conforming strictly to that portion of By-law VIII. which requires the Auditors to report to the Council at least one week before the Annual General Meeting. In future, therefore, the Treasurer will present his Accounts at the Annual Meeting made up to December 31st, instead of to some indeterminate day near the end of March, and these Accounts will be drawn up in a somewhat different form from that previously adopted. A statement of the financial condition of the Society made up for the year ending December 31st last in this modified form accompanies this Report, including a Revenue and Expenditure Account and Balance Sheet, but the Treasurer has considered it advisable on this occasion to include for purposes of comparison another statement made out on exactly the old lines up to March 12th, and it is to this

latter statement, which is comparable with the one of last year, that the following remarks apply:—

The total income of the Society, from March 22nd, 1903, to March 12, 1904, was £7276 16s. 5d., whilst the expenditure for the same period was £6060 17s. 4d., showing an excess of income over expenditure of £1215 19s. 1d., against a surplus last year of £817 7s. 1d. The comparison, however, is not a fair one, unless we adjust the figures in the respective years for the arrears of contributions in each case.

Owing to the alteration in July last of By-law I., by which Fellows who are in arrear with their subscriptions do not receive the publications of the Society, the annual contributions, which become due in January, have been paid up more punctually this year than usual. On March 22nd, 1903, the arrears amounted to £2316, whilst on March 12th this year they were £2008, a difference in favour of this year of £308. When this adjustment is made, the surplus of this year becomes £907 19s. 1d. against £817 7s. 1d. last year, a result which may be regarded as highly satisfactory when we take into consideration certain large items of extraordinary expenditure which have been incurred this year, and which will be alluded to later.

The total amount received this year for Admission Fees, Life Compositions, and Subscriptions is £5809 against £4776 last year, a difference in favour of this year of £1033. This, however, includes £250 received on Account of Arrears of Subscriptions from the late Assistant Secretary, and, as already stated, the subscriptions this year are paid up more closely by £308. With these adjustments, the increased income this year from contributions of Fellows is £475, about half of which is due to the unusually large number of Life Composition Fees.

The sale of the Society's publications, and the proceeds of the advertisements in the *Journal* have brought in £40 19s. 4d. more than last year.

With regard to investments, the Treasurer has to report that since the last General Meeting he has, with the authority of the Council, purchased on behalf of the Society £1500 of Transvaal 3 per cent Guaranteed Stock. The investments on the General Account now stand at £18,009 5s. 5d., whilst those of the Research Fund Account are valued at £6659 3s. 5d.

The total expenditure this year shows the large increase of £665 19s. 4d., which is due to certain large items of an exceptional nature.

The balance of the cost of the first volume of the Decennial Index, 1893-1902, amounting to £386 9s. 7d., is chargeable against this year's revenue, being an increase of £254 5s. 3d. The completion of the Library Catalogue was announced in the Report of last year, but the main cost of £156 16s. 0d. has been borne by the present accounts. The additional accommodation for books referred to in an earlier part of this Report has been provided at a cost of £128 2s. 4d. Two other large items of expenditure of an exceptional nature amounting to £228 1s. 6d. are included under Accountants' and Legal charges, and are mainly attributable to a special investigation of the Society's Accounts to 1895, to which reference has already been made.

It is satisfactory to notice that the expenses incidental to the publication of the *Journal* show a decrease this year of about £100.

The system of keeping the Treasurer's accounts has undergone revision during the past year, the old system having been found insufficient for the present needs of the Society.

At the request of the Council, Messrs. W. B. Keen and Co., Chartered Accountants, have opened up a new set of books, and have also undertaken to give the Treasurer a quarterly audit, and to assist in the preparation of the accounts for the Annual Statement.

This arrangement, which guarantees skilled professional assistance and a thorough checking of the accounts at frequent intervals, has now been in operation for some time, and will not entail any additional expense to the

Society, as the appointment of a Treasurer's Assistant is thereby rendered unnecessary.

Arrangements have been made with Messrs. Coutts and Co., the Society's Bankers, by which in future they will receive the contributions of Fellows direct.

Prof. H. B. DIXON moved the adoption of the report, which was seconded by Mr. E. W. VOELCKER, and carried unanimously.

Dr. SCOTT proposed, and Dr. PHILIP seconded a vote of thanks to the Auditors, which was acknowledged by Dr. MOODY.

The PRESIDENT then delivered his Address, which was devoted chiefly to a review of the scientific history of the Society since its foundation in 1841. The early volumes of the Memoirs of the Society contain papers by many eminent foreign chemists, such as that on "The Atomic Weight of Carbon," by Professors Redtenbacher and Liebig, and the memoir on "The Radical of the Cacodyl Series," by Professor Bunsen. These and others, such as Frankland's paper on "The Isolation of the Organic Radicals," indicate the general nature of the problems which occupied chemists in the early days of the Society. The *Quarterly Journal*, which, in 1849, succeeded the three volumes of Memoirs, contain many contributions by Hofmann, Williamson, Frankland, Kolbe, and Odling, but as it was the custom in those days for authors to send all their serious work to the Royal Society, the *Journal of the Chemical Society* does not provide a continuous picture of the results of chemical investigation in this country. In 1862, the *Quarterly Journal* was replaced by a monthly issue, and in 1863 a new series was commenced.

At that period, language and formulae were alike governed by the then predominant theory of types. Modern views of constitution based on clearer ideas of valency were not definitely exhibited in the *Journal* till 1865, when Dr. Crum Brown's paper appeared on "The Theory of Isomeric Compounds." The change could, however, be accomplished only after agreement had been arrived at in reference to atomic weights. Stereochemical ideas, inaugurated in 1875 by Le Bel and van't Hoff, have reached their logical conclusion in the work of Pope.

Other subjects traced through the successive volumes of the *Journal* are the spectroscopy, the periodic scheme of classification, molecular weights, and the application of Avogadro's law. The paucity of systematic research in the United Kingdom during so many years was referred to, and some of the causes which led to the publication of so few papers by the Society, and the rapid development of activity during the last twenty years.

The Address concluded with a suggestion for the publication by the Society of annual reports on the progress of chemistry in its several more important divisions.

Prof. EMERSON REYNOLDS proposed a vote of thanks to the President, coupled with a request that he would allow his Address to be printed in the *Transactions*.

Mr. DAVID HOWARD seconded the motion, which was carried by acclamation, and acknowledged by the PRESIDENT.

Prof. DIVERS proposed a vote of thanks to the Treasurer, Secretaries, and Council. This was seconded by Mr. SPILLER and unanimously adopted. Dr. SCOTT responded.

The Scrutators presented their report to the President, who declared the following to have been duly elected as Officers and Council for the ensuing year:—

President—W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents who have filled the office of President—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; W. H. Perkin, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J.

Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—Horace T. Brown, LL.D., F.R.S.; Harold B. Dixon, M.A., F.R.S.; Wyndham R. Dunstan, M.A., F.R.S.; P. F. Frankland, LL.D., F.R.S.; David Howard; Raphael Meldola, F.R.S.

Secretaries—W. P. Wynne, D.Sc., F.R.S., M. O. Forster, D.Sc., Ph.D.

Foreign Secretary—Sir W. Ramsay, K.C.B., LL.D., F.R.S.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Other Members of Council—Augustus E. Dixon, M.D.; J. J. Dobbie, M.A., D.Sc.; Bernard Dyer, D.Sc.; Alfred D. Hall, M.A.; A. Harden, D.Sc., Ph.D.; J. T. Hewitt, M.A., D.Sc.; C. A. Kohn, Ph.D., B.Sc.; A. Lapworth, D.Sc.; J. E. Marsh, M.A.; E. J. Mills, D.Sc., F.R.S.; S. Ruhemann, M.A., Ph.D.; J. M. Thomson, LL.D., F.R.S.

Errata.

P. 141, col. 2, the formula at foot should read " $\text{CO}_2\text{H}\cdot\text{CH}\cdot$," &c. P. 142, col. 1, line 21, read "cis- α -hydroxyhexahydroterephthalic acid."

The Faraday Lecture.

The Faraday Lecture will be delivered by Prof. W. Ostwald on Tuesday, April 19th, 1904, at 8.30 p.m.

Prof. Ostwald will lecture in English, the subject of his discourse being "Elements and Compounds."

The lecture will be delivered, by the kind permission of the Managers, in the Theatre of the Royal Institution, 21, Albemarle Street, W.

NOTICES OF BOOKS

Mineral Tables for the Determination of Minerals by their Physical Properties. By ARTHUR S. EAKLE, Ph.D. First Edition, First Thousand. London: Chapman and Hall, Limited. New York: John Wiley and Sons. 1904. Pp. 73.

These tables will be found very useful for reference in the determination of minerals by means of their physical properties; they include the common minerals and a few others of local prominence which are generally looked upon as rare. The minerals are arranged primarily according to streak and "color" (the book being printed in the United States), and under each "color" the arrangement is according to hardness. The other properties tabulated are composition, lustre, system of crystallisation, cleavage or fracture, specific gravity, and common structure, with a final column for remarks and observations. There are a few preliminary pages describing all the properties in detail, and giving an analytical key; there is also a full index.

X-Rays Simply Explained: a Handbook on the Theory and Practice of Radiography. By R. P. HOWGRAVE-GRAHAM, Assoc.I.E.E. Fully Illustrated, with Six Full-page Plates. London: Percival Marshall and Co. Pp. 93.

WHILE intended specially for students and amateurs, this book will also be of use and interest to the practical man. As the author very wisely puts it, "the mere production of fairly good radiographs does not entitle a man to call himself practical; unless he understands some of the principles which underlie the work he is more hopelessly unpractical than he who is frankly and modestly ignorant." In these pages the author gives a thorough description of the principles involved in Röntgen, or X-ray, work, and of the use and management of the apparatus employed, including the taking of radiographs and the construction of fluorescent screens. At the end of the book there are half-a-

dozen good radiographs illustrating different methods of procedure, but there is no index.

A Treatise on the Theory of Solution: Including the Phenomena of Electrolysis. By W. C. D. WHETHAM, M.A., F.R.S. Cambridge: At the University Press. Pp. 488.

As the use of modern thermodynamic methods, founded on the investigations of Willard and Gibbs, is extending to almost all branches of this subject, and as such methods are still unfamiliar to many students of chemistry and physics, the author has very wisely written an introductory chapter explaining the thermodynamic principles which are applied in the body of the work. In succeeding chapters he deals with the phase rule and its applications to systems of one, two, and three components.

The general problem of solubility is first dealt with in Chapter IV., and in Chapter VII. we come to a consideration of the theories of solution; with regard to the conclusions arrived at by the author as to the nature of solution, he points out that there are two different views, each offering a reasonable explanation of the phenomena. He says:—"At first sight the idea of molecular bombardment on the walls of the membrane by solute particles which are dynamically independent of the solvent molecules seems diametrically opposed to the hypothesis of chemical combination between them; but we know too little about the nature of chemical affinity to be quite sure that it is not due to some relation in the dynamical properties of the reagents, and the two views of solution may after all be different statements of the same truth."

In Chapter VIII. the subject of electrolysis is attacked, commencing with its history, Faraday's work, and the nature of ions. The conductivity of electrolytes and the nature of galvanic cells form the subjects of Chapters IX. and X., and in Chapter XII. we come to the theory of electrolytic dissociation. The final chapters on "Diffusion in Solutions" and "Solutions of Colloids" complete a work which will rank among the foremost of those written on this subject. It is to a great extent mathematical, but the theories and hypotheses put forward by the author are dealt with in a very clear and interesting manner, so that those who are not really mathematicians can follow the subject with profit and pleasure.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 11, March 14, 1904.

Solubility of Silicon in Zinc and Lead.—Henri Moissan and F. Siemens.—Silicon dissolves in zinc at a much lower temperature than in lead. The solubility starts at about 550°. At a temperature of 850°, 1.62 per cent is dissolved. An examination of the form of the curve of solubility shows that about 850° the solubility increases very rapidly, but the authors' experiments would not allow of concordant determinations above this temperature—the boiling-point of zinc being 920°, according to M. Berthelot. In the case of lead, the solubility of silicon starts at a higher temperature, 1100°, and even at 1400° only 0.15 per cent is dissolved. Finally, at the boiling-point of lead, only 0.79 per cent is dissolved. The authors also find that the silicon separates on cooling in the form of crystals possessing all the properties of this metalloid, and whose density is constant and very near the normal density of silicon.

A New Method of Preparation of Calcium Carbide.—Henri Moissan.—In all former experiments the author proved that carbon only reduces lime at a very high temperature, when the latter substance has just attained the liquid state. This condition necessitates the use of the electric furnace for the commercial preparation of calcium carbide. He proves, however, that metallic calcium combines with lamp-black at a dull red heat to form pure calcium carbide, crystalline and transparent. His present research is on the most convenient method of producing the calcium required in this preparation by the electrolysis of calcium chloride or of a mixture of chloride and fluoride of calcium.

An Apparatus for Regulating the Action of Vacuum Pumps.—J. Meunier.—The author draws and describes an apparatus for regulating the action of vacuum pumps.

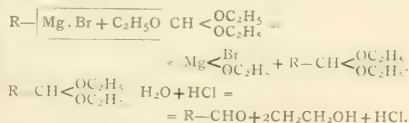
Action of Carbonic Acid on Solutions of Sodium Nitrite.—C. Marie and R. Marquis.—By various experiments on the action of carbon dioxide on solutions of sodium nitrite, the authors find that, in a solution of sodium nitrite containing carbonic acid, there is always a certain amount of free nitrous acid present. Even though the quantity is extremely small, too small to affect the ordinary tests for the acid, the fact remains that this mixture conforms to the general laws of the equilibrium between electrolytes (action of an acid on the solution of a neutral salt).

Method of Preparation of Aldehydes, and the Methodic Degradation of Acids.—E. E. Blaise.—The author finds that the preparation of aldehydes by decomposition of α -oxyacids under the influence of heat is perfectly general, as he shows by various examples, and can be employed for the preparation of all aldehydes containing C_{n-1} , corresponding to a fatty acid containing C_n . In particular, he applies this method to the preparation of aldehydes of moderate and high atomic weight, to obtain which the corresponding primary alcohol does not constitute an accessible primary substance. Finally, the distillation of α -oxyacids constitutes the best method of methodic degradation of acids by the following series of reactions:—



The advantage of this method of degradation consisting in its easy execution, in the easy isolation in the pure state of the intermediate products, and finally in the good yields obtained.

A General Method of Synthesis of Aldehydes.—F. Bodroux.—In a preceding research the author showed that the action of ethyl-ortho-formate on aromatic organo-magnesium compounds in ethereal solution gives rise to the aldehydes—



He applies these reactions to various compounds, and finds this a convenient method of synthesising aldehydes.

Certain Derivatives of α -Campholytic Acid and α -Campholenic Racemic Acid.—G. Blanc and M. Desfontaines.—Continuing the experiments made by M. Blanc, both alone and in collaboration with M. Blaise, to prove α -campholenic and α -campholytic acids to be homologous, the authors now prepare the campholytic nitrile, unknown up to the present time. They then reduce the nitrile and compare the base obtained with α -racemic aminocampholene. Apparently these two bases are dif-

ferent. When the two ureas and the two oxamides are mixed, after crystallisation they obtain products which melt respectively at 114° and 130° . It therefore appears that the base obtained by reduction of the α -campholytic nitrile is impure α -aminocampholene, the nitrile not being a homologous body.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 11th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The Right Hon. the Marquis of Salisbury, Mr. W. B. Anderson, Mr. J. Benson, Mrs. G. E. Bröun-Morison, Mrs. Douglas Cow, Mrs. J. Mackenzie Davidson, Mr. J. A. W. Dollar, Mr. Bayntun Hippisley, Mr. E. W. Linging, Mrs. Master, Mr. J. C. Prince, Mr. E. A. Short, Mr. H. L. Tidy, Mr. W. Watson-Taylor, and Mr. C. S. Whitehead were elected members. The special thanks of the members were returned to Mr. Francis Gaskell for his donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures.

Institute of Chemistry of Great Britain and Ireland.—The next Examinations for persons desirous of qualifying themselves to be public and technical analysts, will be held in July, 1904. The Examinations are open only to candidates who have complied with the regulations. The Intermediate Examination will be held in the Laboratories of the Institute, commencing on Tuesday, the 5th of July. Examinations in the following branches of the Final Examination for the Associateship (A.I.C.) will also be held in the Laboratories of the Institute, commencing on either Tuesday, the 5th, or Tuesday, the 12th of July:—(a) Mineral Chemistry, (b) Metallurgical Chemistry, (c) Physical Chemistry, (d) Organic Chemistry, and (e) The Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy. Applications for admission to the July Examinations should be forwarded to the Registrar not later than Tuesday, the 7th of June, 1904, on which day the List of Candidates will be closed.

MEETINGS FOR THE WEEK.

TUESDAY, 19th.—Royal Institution, 5. "The Transformations of Animals," by Prof. L. C. Miall, F.R.S.

Society of Arts, 8. "The Sentiment of Decoration," by Alred East, A.R.A.

WEDNESDAY, 20th—Society of Arts, 8. "Motor Cars for Popular Use," by Mervyn O'Gorman, M.Inst. E.E.

Microscopical, 8. Exhibition of Pond Life.
Chemical, 5.30. "Vapour Density of Hydrazine Hydrate," by S. H. C. Briggs. "Experiments on the Synthesis of the Terpenes—Part I, Synthesis of Inactive Terpineol, of Dipentene, and of Terpin Hydrate," by W. H. Perkin, jun. "A Levo-rotatory Modification of Quercitol," by F. B. Power and F. Tutin. "Constituents of the Essential Oil of Californian Laurel," by F. B. Power and F. H. Lees. "Some Derivatives of Umbellulone," by F. H. Lees.

THURSDAY, 21st.—Royal Institution, 5. "Dissociation," by Prof. Dewar, F.R.S., &c.

FRIDAY, 22nd.—Royal Institution, 9. "Sleeping Sickness in Uganda," by Col. David Bruce, R.A.M.C., F.R.S.
Physical, 5. "Calculation of Colours for Colour Sensitometers, and the Illumination of 'Three Colour' Photographic Transparencies by Spectrum Colours," by Sir W. de W. Abney, F.R.S. "On Normal Filing as connected with Osborne Reynolds's Theory of the Universe," by Prof. J. D. Everett, F.R.S. "Note on the Diffraction Theory

of the Microscope as applied to the case when the Object is in Motion," by Dr. R. T. Glazebrook, F.R.S. Exhibition of Apparatus by Peter Heele.

SATURDAY, 23rd.—Royal Institution, 3. "Cameos," by Cyril Davenport, F.S.A.

THE CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

Five lines in column (about 10 words to line)	4 s. d.
Each additional line	0 3 6
Whole column	1 15 0
Whole page	3 0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.



OLD PLATINUM

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and Purchased

IMPERIAL COLLEGE OF CHEMISTRY,

49 & 51, IMPERIAL BUILDINGS, LUDGATE CIRCUS, E.C.

Principal—FREDERICK DAVIS.

PRACTICAL AND THEORETICAL TUITION

in Botany, Chemistry, Pharmacology, and Therapeutics for All Medical and Science Examinations.

Especially Course of Instruction in Therapeutics, Pharmacology, and Microscopy for Institute of Chemistry Exam.



SPINTHARISCOPES

AS DEvised BY
SIR WILLIAM CROOKES.

Showing the Scintillations of Radium

PRICE WITH LENS . . . £1 1s.
FOR MICROSCOPE . . . 10s. 6d.

A. C. COSSOR,
54, FARRINGTON ROAD, E.C.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2317.

THE SOLUBILITY OF SOME SALTS OF THE LOWER FATTY ACIDS.

By H. STANLEY, B.Sc. (Lond.).

LUMSDEN (*Trans. Chem. Soc.*, 1902, 355) has determined values for the construction of the solubility curve for (amongst others) calcium formate. It was thought that the curves for the barium and strontium salts of the same acid might prove of interest, and possibly also that they would show similarity to a gradation from the calcium formate curve, when these elements are looked on as member of the same group in Mendeleeff's Periodic System. The calcium salts of the lower and more soluble ones of the series are noteworthy as exhibiting a decrease in solubility with rising temperature, and the barium and strontium salts might reasonably be expected to show some such deviation from the ordinary type of solubility curve, the equation to which may be given in some such form as—

$$S = a + bt,$$

where t is the temperature.

The calcium formate curve is practically a straight line, similar to those for potassium chloride, sodium nitrate, and some other inorganic salts.

Some salts of the lower fatty acids have been prepared, and their solubilities determined; below are given the results obtained for the three formates. Only three points on the calcium curve were determined, the values not showing any appreciable difference from those obtained by Lumsden.

Preparation of the Salts.

The method adopted was the same in all cases, viz, by adding excess of the powdered carbonate to the acid, suitably diluted with water, warming, filtering, and concentrating the filtrate by evaporation to obtain the salt in crystalline form.

Barium Formate.—Forms monoclinic prisms, insoluble in alcohol or ether; contains no water of crystallisation.

0.9937 grm. gave 1.0027 grm. $\text{BaSO}_4 = 59.82$ per cent Ba.
 $\text{Ba}(\text{HCOO})_2$ requires 60.46 per cent Ba.
 $\text{Ba}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ requires 56.04 per cent Ba.

Strontium Formate.—Forms rhombic crystals exhibiting hemihedral forms (Pasteur, *Ann. Chim. Phys.*, [3], xxxi., 98; Jacobson, *Pogg. Ann.*, cxlii., 493), insoluble in alcohol or ether. It crystallises with two molecules of water, in this respect differing from the corresponding salts of barium and calcium. The propionate and acetate of strontium also contain more water of crystallisation than do those of barium and calcium.

0.7391 grm. gave 0.904 per cent Sr.
 $\text{Sr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ requires 41.09 per cent Sr.

Solubility Determination.

The solution, with excess of solid, was contained in a stout bottle, with a doubly bored rubber stopper, admitting a stirrer rotated by means of a water turbine, and a tube leading to a second vessel, into which as much solution as was required could be drawn off for analysis. A thermometer reading to tenths of a degree was used, and it was found possible with the regulator employed to keep the temperature constant, usually to one-tenth, and always to one-fifth of a degree for the requisite length of time. As the saturation point was approached, more of the solid in a finely powdered state was added, as recommended by Ostwald.

Barium Formate, $\text{Ba}(\text{HCOO})_2$.

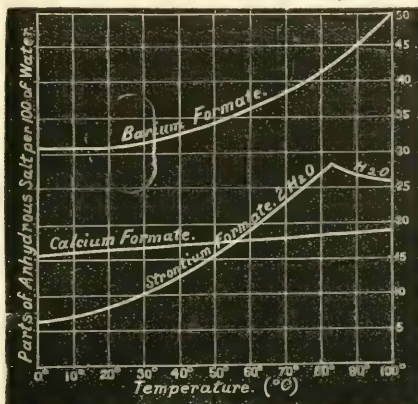
Temp. °C.	Weight of solution.	Weight of BaSO_4 .	Weight of Ba formate.	Weight of water.	Per cent Ba formate.
0.0	1.0964	0.2602	0.2553	0.8431	30.28
10.0	1.3951	0.3340	0.3254	1.0697	30.41
35.0	2.1230	0.5333	0.5195	1.6035	32.32
54.5	1.4630	0.4012	0.3908	1.0722	36.36
73.6	2.5780	0.7425	0.7233	1.8447	39.31
93.2	2.5503	0.8280	0.8067	1.7431	40.25
100.0	2.8625	0.9310	0.9070	1.9555	48.88

Strontium Formate, $\text{Sr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$.

Temp. °C.	Weight of solution.	Weight of SrSO_4 .	Weight of Sr formate.	Weight of water.	Per cent Sr formate.
0.0	3.8869	0.3356	0.2550	3.6319	7.02
11.0	5.3809	0.5309	0.4033	4.9776	8.08
28.6	1.5023	0.2058	0.1564	1.3459	11.62
37.4	1.9733	0.2995	0.2281	1.7452	13.01
51.4	2.1848	0.4031	0.3036	1.8812	16.31
67.5	1.6596	0.3735	0.2838	1.3758	20.62
81.5	3.1110	0.8480	0.6445	2.4665	26.14
86.0	1.5121	0.4312	0.3277	1.1844	27.58
91.7	1.6831	0.4711	0.3581	1.3250	27.01
100.0	2.8097	0.7762	0.5899	2.2198	26.57

Calcium Formate, $\text{Ca}(\text{HCOO})_2$.

Temp. °C.	Weight of solution.	Weight of CaSO_4 .	Weight of Ca formate.	Weight of water.	Per cent Ca formate
0.0	1.0000	0.1600	0.1600	0.8400	16.00
51.7	1.0000	0.1732	0.1732	0.8268	17.32
100.0	1.0000	0.1829	0.1829	0.8171	18.29



Considerable difficulty has been experienced in getting definite values for the barium acetate curve, and the results are not yet complete. The author's best thanks are due to Mr. E. C. Martin, B.Sc., for help with this part of the work, and also to Prof. Wertheimer for granting the use of the research laboratory at the College.

Merchant Venturers' Technical College,
Bristol.

Directory of Paper Makers of the United Kingdom.

—We have just received the 1904 edition of this Directory, in which the list of paper makers of the United Kingdom has been carefully and authentically revised. Additions have been made to the list of trade designations used as water-marks, &c., bringing the total to over 5500; there is also a complete classification of advertisers, forming a directory of paper makers' principal engineers, purveyors of raw materials, &c., which will be of great use to those engaged in the trade. The Directory comprises 192 pages.

THE ELEMENTS: VERIFIED AND UNVERIFIED.

By CHARLES BASKERVILLE, Ph.D., F.C.S., Smith Professor of General Chemistry, University of North Carolina

(Continued from p. 187).

LIST OF PROPOSED CHEMICAL ELEMENTS (continued).

Date.	Name.	Source.	Authority.	Reference.	Remarks.
1898	Radio-active thorium (Thorium X).	Pitchblende.	Curie and Schmidt (independently).	Wied. Ann., 65, 141; Mdm. Curie's thesis, Faculté des Sciences de Paris, 1903, (Chem. News, 88, 85).	See also Crookes's Thorium X and Rutherford's Thorium X. All likely same. Characteristic "emanations," perhaps due to helium (see Soddy and Rutherford, and Ramsay, Chemical News, 1903). Giesel says radio-activity not due to actinium (Berichte, 34, 3776). See Hofmann and Zerbán.
1898	Coronium.	Fumarole gas.	Nasini, Anderlini, and Salvadori.	Atti R. Acad. dei Lincei, Roma, [5], 7, 14, 73; Chemical News, 78, 43.	Spectra of gases from Solfatara di Pozzuoli and Vesuvius fumaroles showed, besides argon (λ 531.5) and other lines, 1474 K, attributed to the corona, hence terrestrial coronium.
1898	KRYPTON.	Liquid air.	Ramsay and Travels.	Proc. Roy. Soc., 63, 405.	See special works on these novel constituents of the air; also Ladenberg and Krugel.
1898	NEON.	Liquid air.	Ramsay and Travels.	Proc. Roy. Soc., 63, 437.	Predicted by Johnstone Stoney from mathematical calculations; and Ramsay (Presidential Address to the Chemical Section of the British Association, Toronto Meeting, 1898).
1898	XENON.	Liquid air.	Ramsay and Travels.	Chemical News, 78, 154.	Very heavy gas.
1898	Metargon.	Liquid air.	Ramsay and Travels.	Trans. American Assoc. Adv. Science, Boston Meeting; Chem. News, 78, 197.	Subsequently shown to be carbon monoxide.
1898	Etheron.	Liquid air.	Brush.		Calculated atomic weight 0.001 ($H = 1$). Crookes attributes the observations to watery vapour. A personal letter assures me he is still busy with the problem and "building a very large and elaborate apparatus for separating minute quantities of very light gases."—C. B.
1898	Polonium.	Pitchblende.	Curies.	Comptes Rendus, 127, 1755; 134, 85.	Radio-active bismuth. Precipitated by hydrogen sulphide from acid solution. See also Giesel (Wied. Ann., 1899, 69, 84) and Markwald (Berichte, 1902, 35, 2285).
1898	RADIUM.	Radio-active barium in pitchblende.	Curies.	Comptes Rendus, 127, 1225; 129, 717; Wied. Ann., 1900, 2, 742.	By prolonged fractional crystallisation of chlorides and bromides characteristic spectrum, as shown by Demarçay, Runge and Exner, and Crookes (Chemical News). For full account of this wonderful substance see Mdm. Curie's thesis, "Radio-active Substances" (Chemical News, 88, 85 <i>et seq.</i>); Giesel, "Die Radio-activen Stoffe, &c.," Hofmann, "Radio-activity and Chemistry"; Barker; and numerous papers in the journals.
1899	Actinium.	Pitchblende.	Debierne.	Comptes Rendus, 129, 593; 130, 906.	Resembles titanium in iron group. See full papers, and works of Hofmann and Zerbán (Berichte, 1902, 35, 53); Baskerville (Journ. Am. Chem. Soc., 23, 764), and Brauner (Proc. Chem. Soc., 17, 67). No doubt new element. Must not be confounded with Puppon's actinium. See Uranium X.

1899	Asterium hydrogen (new). Unknown.	Stars of different temperatures.	Lockyer.	Royal Society, February 23, 1899; Chemical News, 1899, 79, 145.	Dependent upon spectroscopy. See original paper for wave-lengths and range of stars in which the several lines may be seen. See also Pickering's "New hydrogen."
1899	VILTRORIUM. (Monium).	Yttria.	Crookes.	Chemical News, 79, 212; 80, 49.	First called "Monium." Atomic weight and spectrum criteria (also phosphorescent). Obtained by prolonged and varied fractionations of yttrium salts. Atomic weight 117.
1900	Uranium X.	Uranium.	Crookes.	Proc. Roy. Soc., 1900, 407.	Doubtless Debierne's actinium. Hofmann and Zerban (loc. cit.) maintain minerals freed from uranium give a non-active thorium. The whole problem of radio activity is open. Strutt secured strong radio-active gas from mercury (Phil. Mag., 16, 6, 113); Wilson showed fresh snow gives radioactive residue on evaporation (Proc. Phil. Soc. Camb., 1903, 2, 85; Geisel (Ann. Physik., 1903, 41, 10, 449); &c.
1900	Thorium .. Thorium X.	Thorium.	Brauner.	Proc. Chem. Soc., London, 17, 67.	Hydrolysis of hepta-hydrated thorium tetra-ammonium oxalate. One with atomic weight 220; other, 260. No doubt one method, but slow at breaking thorium into its constituents. See Baskerville. Auer says quite possible thorium is not an element (Chemical News, 85, 255; Journ. f. Gas Beleucht. u. Wasservers., 1901, 661). Drossbach analysed two commercial thorium nitrates and found small amounts of different rare earths present (Zeit. f. Angew. Chem., 14, 655). He accounts for Brauner's observations by presence of ytterbium.
1900	f Δ α φ	Terbia.	Demarcay.	Comptes Rendus, 131, 6; Chemical News, 82, 127.	Δ may be de Boisbaudran's Z ₇ . Characteristic spectral lines. Unsettled so far.
1900	Krypton II.	Liquid air.	Ladenberg and Krugel.	Akad. d. Wiss. Berlin; Chemical News, 82, 269.	850 litres liquid air distilled. Molecular weight obtained = 58.81.
1900	Austrium II.	Orthite.	Pribram.	Monats., 1900, 21, 148—155; Journ. C. S., 77—8, 3, 347.	See Linnemann. He found traces of a new element, quite distinct from Linnemann's; yet to be isolated. Independently of Brauner. Pure thorium fractioned by precipitation with sulphur dioxide, &c. Variation in atomic weights (225 for 232.6). Heavy constituent more radio-active than other, judged by photographic and electrical methods. Later work, fractioning by organic bases and distillation of chloride. Show three elements present—carolinium, true thorium, and berzelium (see).
1900	Carolinium.	Thorium.	Baskerville.	American Chemical Society, North Carolina Section, April, 1901; Journ. Am. Chem. Soc., 23, 761; Chemical News.	(see). Doubtless Thorium X of Crookes and Rutherford is the radio-active element present accumulating with the carolinium. It does not necessarily follow that carolinium is radio-active, although the active body accumulates with it.
1900	Radio-active tend.	Brggerite.	Hofmann and Strauss.	Berichte, 1901, 33, 3129; 34, 907; 1902, 35, 1453; &c.	Primarily active substance. They state perhaps two elements present with atomic weights 100.9 and 171.96.
1901	"2" EUROPTIUM.	Samarskite.	Demarcay.	Comptes Rendus, 132, 1484;	Atomic weight 151, characteristic spark spectrum. Phosphorescent spectrum shows it to be Crookes's S ₆ , and reversal spectrum de Boisbaudran's Z ₅ .

OBSERVATIONS ON
SOME CONTINUOUS INTRAMOLECULAR, AND
AT FIRST REVERSIBLE, CHANGES
EXTENDING OVER PROLONGED PERIODS
OF TIME.

By R. J. FRISWELL.

PART I.

It had long been held, though until the liquefaction of the so-called permanent gases there was no experimental proof, that at a temperature approaching the absolute zero changes would be completely inhibited in bodies subjected to it, whilst, on the other hand, many years of work on the spectra of the sun and the fixed stars have proved that there is also an upper limit to such changes. Grove had arrived at the latter conclusion as far back as 1846, as a result of his work on the combination of hydrogen and oxygen by heat and electricity, and the decomposition of water by heat. (See *Phil. Trans.*, 1847, Bakerian Lecture, dated August 26, 1846, Supplement, November 10, 1846, "On certain Phenomena of Voltaic Ignition and the Decomposition of Water into its Constituent Gases by Heat." P. 15.—"If therefore there be planets whose physical condition is consistent with intense heat, the probability is that the substances that compose them are in a totally different chemical state from ours, and resolved into what we call elements, but which by intense heat may be again resolved into more subtle elements." P. 19.—"there appears to be an extensive series of facts which afford strong hope of a generalised antagonism between thermic repulsion and chemical affinity, and a consequent establishment of the law of continuity in reference to physical and chemical attraction").

Between the very wide range of temperature here assumed, changes of all degrees of rapidity occur, and for obvious reasons investigators have concerned themselves with such as take short spaces of time. They have also almost always endeavoured to hasten them, looking more to final results than to the transition products arising during molecular interchange.

This has, I think, caused slow changes to be neglected, and has a tendency to regard substances as of far greater rigidity or stability than they really possess.

Of course much work has been done pointing in another direction, and of this none has been more remarkable than that of Roberts-Austen on the transfusion of metals.

A full realisation of the state of nature thus exhibited experimentally appears to do away with much of the apparatus, often cumbersome and unwieldy, brought in to account for changes, such as electro-chemical force, reversed electrolysis, and so on.

The energy of chemical change can be measured in terms of electrical phenomena, just as the change in the position of a body in relation to the centre of the earth can, the explanation being simply a re-statement of the doctrine of the conservation of energy.

The tendency of explanations such as the above has also been to induce a strongly held belief in the constancy of atomic constitution, or rigidity of configuration of the molecules of substances, change being looked on as arising from without the molecule.

Many years since, to account for the change of diazobenzeneanilide into aminoazobenzene, V. Meyer proposed the theory of the "labile" or movable hydrogen atom (*Ber.*, xiv., p. 2447). The view advocated attracted attention for a time, but has been somewhat overlooked amidst the growth of stereo-chemical theory.

This reaction was subsequently investigated by Friswell and Green, who showed that the cause was slight dissociation of the diazobenzeneanilide into diazobenzene and aniline (of course in the form of their salts) brought about by dilute hydrochloric acid (*Trans. Chem. Soc.* xvii., 917; xlix., 746).

Give this condition sufficient time and a favourable tem-

perature, the bodies re-arrange themselves into the molecule known as aminoazobenzene hydrochloride. It seemed, therefore, that it should be possible to produce aminoazobenzene hydrochloride directly, since the diazobenzene anilide was resolved into diazobenzene and aniline as a preliminary to its formation. But every attempt failed, and we proved that under all conditions known to us diazobenzene and aniline combined first into diazobenzene anilide, and that diazobenzene anilide then split up into diazobenzene and aniline, which very slowly combined into the aminoazobenzene molecule.

The experiments to be detailed in the second part of this paper throw a considerable light on this process, since aminoazobenzene is shown to be a base capable of decomposing aniline hydrochloride, while in the papers quoted it is shown that hydrochloric acid dissociates diazobenzene anilide into diazobenzene and aniline.

The whole of the molecules being in such a solution in a state of strain there is but one way of releasing the tension, and that is by the formation of a *basic* body capable of saturating hydrochloric acid.

As might be expected, there is a degradation of energy, the violently explosive diazobenzene anilide having become the stable aminoazobenzene.

The molecules have released to some extent their atoms, the system is, so to speak, in a nebular state; throw an appropriate strain on these wandering atoms, and you can compel them to assume certain configurations, by which the fact of their wandering is diagnosed, the diagnosis taking the form of an assertion of the presence of one of the complexes originally employed.

In the case before us, diazobenzene anilide is formed, and in the absence of an acid will continue to exist, the body being in fact an aniline salt, and since the diazobenzene is the more chlorous or negative portion of the molecule, it should be called aniline diazobenzide. An acid strain thrown on to it will cause its conversion into a *basic* body as a whole, provided the acid is one which is of so powerfully acidic a character as to be able to break up the whole mass into a salt of aniline and a diazobenzene salt, and thus exclude the latter from all participation in the reaction. I would venture to suggest, in view of these results, that the character of a chemical body is a function of the strains mutually exerted between it and the reagents we make use of to "ascertain its constitution." Applying a different strain, we should assume a different constitution.

Hence there is no incongruity in bodies having two or more formulæ or playing according to circumstances two parts, as, for instance, both that of base and acid, as certain hydroxy-amino compounds certainly do.

Moreover, in the case of such bodies, the greater the acid character of the acid brought into contact with them the greater is the development of the basic power of the other member of the complex, and, conversely, the less the power of the acid the greater the acid or phenolic properties.

Thus it may be safely said that the character of the body is a function of its environment, and here again we get a difference strongly separating a chemical molecule from a rigid system.

I am therefore led to hazard the hypotheses:—

- I. That V. Meyer's "labile" or movable hydrogen atom is not the only atom endowed with variability.
- II. That "constitution" is the constitution of a substance when subjected to a particular strain.
- III. That the properties of a substance are dependent to a greater or less degree upon the body with which its properties are being explored, e.g., one showing but feeble basic properties to a weak acid may, and does, develop strongly basic properties to a strong acid, and *vice versa*.

In support of the above speculations, which have arisen during a very prolonged study of the question, I beg to detail the following experiments which have extended over a long

series of years. The changes occur so slowly that months and even years may pass and still leave them incomplete.

In certain cases it will be shown that the changes can be reversed by a momentary exposure to heat, although a secondary change which always follows the first is brought about in a few hours if the heat be continued; while this change will take about two years to become perceptible, and nearly or quite four to complete if the temperature remains at or about 15° C.

(To be continued).

NOTE ON SCALE FOR CHEMICAL VALUATION OF SOILS.

By VINCENT EDWARDS, F.C.S., F.I.C.

In a recent article on the rapid analysis of soils, I ventured to suggest a plan by which the fertility from a chemical point of view could be conveyed by a given number. At present among those who are interested in soils, there is considerable confusion of terms, vague expressions such as "great fertility," "virgin," "moderate," and so on, are freely used, and as a simple concrete expression seems to be desirable I venture to propose the following plan:—I would describe a good soil as containing 0.25 per cent of each of the three essential ingredients, nitrogen, phosphoric acid, and potash; thus, the three added together, 0.75 would equal 100, and from their analysis all soils could be in a manner compared with the "standard" imaginary one.

It might be objected that certain ill-balanced soils could not be so valued; for instance, a peat soil with excess of nitrogen. I would meet this by, as it were, only giving 25 "marks" for each ingredient. Let us suppose the peat soil contained 2 per cent nitrogen and traces of phosphoric acid and potash; this would therefore be rated at 25 on the scale for the nitrogen alone. A word of explanation, "peaty," and this figure would convey much information.

I am quite aware of the objections to this plan, but I think it does something to remedy the present confusion, and would give some information to those who have not made a study of the constituents of soil, bring them in touch with analytical chemistry, and perhaps encourage them to attempt improvements of sterile conditions with more hope of success. At present the benefits to be derived from agricultural chemistry are a sealed book to vast numbers connected with land, a most melancholy fact. I recently published a "Partial Analysis" of a garden soil containing on the day 0.12 per cent nitrogen, 0.08 per cent phosphoric acid, 0.05 per cent potash; this on the proposed scale would be 33, a figure showing at once some need of rational manurial treatment.

Lawes' Works, Barking.

A NEW PROCESS OF PREPARING VENETIAN RED.

By JOHN GEDDES MCINTOSH.

The following new process of preparing venetian red, recently invented by me, may prove serviceable to those engaged in the industry. It simultaneously solves the question of nuisance from fumes and the admission of air into the furnace. Waste peroxide of lead can be got cheaply, and when it is furnished in molecular proportions with dehydrated ferrous sulphate, after the two have been intimately mixed, the reaction takes place according to the following equation: $2\text{FeSO}_4 + 2\text{PbO}_2 = 2\text{PbSO}_4 + \text{Fe}_2\text{O}_3 + \text{O}_2$, which corresponds to 278 parts of pure $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (green vitriol) to 239 of lead peroxide.

When the proportions are adjusted to a nicely net a particle of fume is given off, and as there is no free acid in

the product it need not necessarily be levigated. If an excess of PbO_2 be used, an equivalent amount of red lead is formed from the peroxide by the escape of oxygen. I commend this process to the notice of the alkali works inspectors as affording a solution of the problem they have been trying to solve this last ten years and more. Should enough lead peroxide not be available for manufacture on the grand scale, partial substitutes may be found in red lead and litharge; or peroxide of manganese could be used, and the resultant MnSO_4 washed out from the Fe_2O_3 . The MnSO_4 could find a ready sale for use in dyeing, and as a raw material in the manufacture of precipitated rosinate of manganese, so erroneously termed resinate of manganese. I am aware that green vitriol has been furnished with either red lead or litharge before now by French chemists, but I do not recollect ever reading of the peroxides of lead and manganese having been used. In the case of the black oxide of manganese the presence of impurities, such as lime, need form no obstacle to the preparation of a pure sulphate of manganese. I have not thought it necessary to patent the processes, which only suggested themselves to me by a client submitting to me a sample of waste lead peroxide to see if I could find a use for it. I tried the above experiments on a large scale, and found them to produce excellent pigments.

Analytical Laboratory,
9, Parsonage Street, Manchester Road,
London, E.

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.*

LANTHANATES.

By CHARLES BASKERVILLE and GEORGE F. CATLETT.

Synopsis.—The resemblance of lanthanum to aluminum was taken advantage of, and the preparation of such bodies as the lanthanates and meta-lanthanates, hitherto not reported, described. The new substances are sodium tetra-lanthanate ($\text{Na}_2\text{La}_4\text{O}_7$) and meta-lanthanates of sodium, potassium, lithium, and barium ($\text{MH}_2\text{La}_3\text{O}_{15}$). Two methods were used: fusion of lanthanum oxide with alkaline carbonates, and prolonged digestion in a concentrated solution of the alkaline hydroxides at 100° C. These bodies do not serve as a means for the separation and purification of lanthanum.

Aluminum, which belongs to the third group in the periodic classification, may be separated from many elements by the solubility of its hydroxide in the non-volatile alkalis. This is due to the formation of soluble aluminates or meta-aluminates. It therefore appeared reasonable that lanthanum, which is classed with the same group, would deport itself similarly and perhaps offer a desirable new mode of separation from other or the rarer elements.

In their work on zirconates, Venable and T. Clarke proposed the following methods for the preparation of this class of bodies (*Journ. Am. Chem. Soc.*, xviii., 5; *CHEMICAL NEWS*, 1896, lxxiv., 42 and 54):—

- I. Fusing with boron trioxide (Ebelmen).
- II. Fusing with alkaline carbonates (Hjortdahl).
- III. Fusing with alkaline hydroxides.
- IV. Fusing with alkaline or earthy chlorides (Hjortdahl).
- V. Precipitation of solutions of salts with alkaline hydroxides (Watts).
- VI. Dissolving the hydroxide in strong solutions of sodium or potassium hydroxide and precipitation by dilution or by neutralisation with an acid.

* From the *Journal of the American Chemical Society*, 1904, xxvi., No. 1.

The process used by Ebelen was not applicable with zirconia, because that oxide does not dissolve in boron trioxide. The second and third processes given above, gave the most successful results. Water and dilute acetic acid were used to dissolve the alkali from the zirconate.

In the work on the lanthanates, those two methods, which were most successfully used by Venable and Clarke, were applied with some alterations, as will be noted in the detailed account which follows. Water was found useless as a washing medium, as, with the exception of the sodium tetra-lanthanate, the other bodies appeared to be decomposed. Acetic acid dissolved the lanthania and supposed lanthanate with equal ease, but it was used effectively in the preparation of the lithium lanthanate. Alcohol was used in most of the experiments, and, as far as could be seen, had little action on the product. In the case of the fusion of lanthania and barium hydroxide, a solution of ammonium chloride in water was used to dissolve out the remaining barium hydroxide.

The lanthanum compounds used were prepared from a quite pure lanthanum ammonium nitrate, generously loaned by H. S. Miner, of the Welsbach Lighting Company. The hydroxide was prepared from this compound by precipitation with ammonia, and washing until free from that volatile alkali. As is well known, lanthanum hydroxide readily absorbs carbon dioxide from the air; hence it was kept covered with water most of the time, filtered, and used fresh in each experiment. The oxide used was obtained by igniting the hydroxide obtained in platinum. Very concentrated solutions (nitrates and chloride, neutral and acid) of varying thicknesses gave no absorption bands, showing the absence of certain of the rare earths that are likely to be present.

The analyses of the preparations were made by dissolving a definite quantity of the dried body in hydrochloric acid, precipitating the lanthanum hydroxide with ammonium hydroxide. The precipitate was thoroughly washed, burned, and weighed as lanthanum oxide. The filtrate was evaporated to dryness, and the alkalis or alkaline earths converted into sulphates, and weighed as such. When water was determined, the material was ignited in combustion tubing and the moisture collected in a tared calcium chloride tube, dry air being drawn through. In several cases, either the washing medium failed to remove all of the carbonate used in the fusion, or some carbonate was formed when the material was exposed to the air. The carbon dioxide was determined in the ordinary alkali-meter by evolution and absorption.

EXPERIMENT I.—Di-sodium Tetra-lanthanate, $\text{Na}_2\text{La}_4\text{O}_7$.

Two grms. of lanthanum oxide and 8 grms. of sodium carbonate were kept in a state of fusion for three hours. The reaction was carried out in a platinum crucible at the temperature of a blast-lamp. At the end of the fusion, it was specked with small yellowish particles, and white crystals were formed. The mass was treated with water until the wash-water was no longer alkaline, corallin being used as indicator. The white crystalline undissolved body remaining was dried at 100° , and, on analysis gave the following results:—

Lanthanum oxide	88.00
Sodium oxide	8.00
Carbon dioxide	2.50
Water (by difference)	1.50

100.00

The carbon dioxide was very probably in combination as lanthanum carbonate, $\text{La}_2(\text{CO}_3)_3$, as sodium carbonate would have been removed by the wash-water. Accounting for the carbon dioxide as being present in this form, we have 8.64 per cent of this carbonate or 91.46 per cent of lanthanum and sodium oxides and water. Disregarding the water and revising the calculations, we have—

Lanthanum oxide	90.99
Sodium oxide	9.00

or the ratio 2 : 1, i. e., $\text{Na}_2\text{La}_4\text{O}_7$, di-sodium, tetra-lanthanate, similar to the boron compound.

EXPERIMENT II.

Hydrated Mono-sodium Poly-meta-lanthanate.

Two grms. of lanthanum oxide and 8 grms. of sodium hydroxide were digested in a silver dish on a water-bath for thirty hours. A white mass, almost insoluble in water but decomposed by it, was obtained. Alcohol was used and the unchanged sodium hydroxide washed out; but not all of the sodium carbonate produced by the absorption of carbon dioxide from the air. The body gave on analysis:—

Lanthanum oxide	79.60
Sodium oxide	2.80
Carbon dioxide	3.00
Water (by difference)	14.6

Providing for the carbon dioxide as in the first experiment, we have $\text{NaH}_9\text{La}_5\text{O}_{15} \cdot 4\text{H}_2\text{O}$, comparable to the poly-meta-stannates in which one of the hydrogen atoms appears to have been replaced by the metal sodium.

EXPERIMENT III.

Hydrated Mono-lithium Poly-meta-lanthanate.

Two grms. of lanthanum oxide and eight grms. of lithium carbonate were fused in a platinum crucible for five hours. Much difficulty was experienced in washing out the alkali, which was eventually removed by careful treatment with 5 per cent acetic acid. The acid was subsequently removed by means of alcohol. A small amount of material insoluble in hydrochloric acid was found when it was examined. The analysis of the white body gave the following results:—

Lanthanum oxide	82.9
Lithium oxide	1.2
Carbon dioxide	4.3
Water	9.8
Body insoluble in hydrochloric acid	1.3

99.5

Allowing carbon dioxide to be combined in the form of lanthanum carbonate, as all of the lithium carbonate was washed out with the acetic acid, we have $\text{LiH}_9\text{La}_5\text{O}_{15} \cdot 2\text{H}_2\text{O}$ similar to the above, with the exception of having 2 molecules of water instead of 4.

EXPERIMENT IV.

Hydrated Mono-potassium Poly-meta-lanthanate.

Two grms. of lanthanum oxide and 16 grms. of potassium hydroxide were digested in a covered silver crucible on a water-bath for thirty hours. It was leached with alcohol, as it was found that water decomposed the material as in the case of the sodium hydroxide digestion. The white body gave, on analysis, the following results:—

Lanthanum oxide	79.50
Potassium oxide	2.53
Carbon dioxide	0.40
Water	18.69

101.12

which approximates the formula $\text{KH}_9\text{La}_{10}\text{O}_{15} \cdot 15\text{H}_2\text{O}$.

The body without doubt was decomposed during the washing; hence no value can be attached to the results obtained by analysis.

EXPERIMENT V.—Calcium Compound.

An attempt was made to fuse calcium carbonate with lanthanum oxide, but such great difficulty was experienced in making the fusion and removing the unchanged calcium salts that the experiments were discontinued.

EXPERIMENT VI.

Barium Poly-meta-lanthanate, $\text{Ba}(\text{H}_9\text{La}_5\text{O}_{15})_2$.

Barium hydroxide was substituted for the sodium hydroxide and the digestion carried out as in the first

experiment. A concentrated water solution of ammonium chloride was used for leaching. The body obtained gave, on analysis:—

Lanthanum oxide	75.97
Barium oxide	6.05
Carbon dioxide	2.8
Water	14.9

99.72

or, disregarding the carbon dioxide, we have $\text{Ba}(\text{H}_2\text{La}_2\text{O}_{15})_2$.

As a result of these experiments, it appears that a number of bodies, quite complex in character, may be had, which seems to show the existence of a series of compounds of lanthanum which may be termed meta-lanthanates or poly-meta-lanthanates. At the same time it is quite evident from this and other work which immediately follows, that the methods are not suitable as a means of separation of these rare earths, and really little value can be attached to the above.

A per-lanthanate, or hydrated peroxide, $\text{La}_2\text{O}_5 \cdot x\text{H}_2\text{O}$, was obtained by fusion with sodium peroxide. Such a body has already been reported by Melikoff and Pissarjewsky (*Zeit. Anorg. Chem.*, xxi., 70).

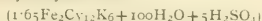
CHEMICAL EQUILIBRIUM BETWEEN THE FERRO- AND FERRI-HYDROCYANIC ACIDS.

By MAURICE PRUD'HOMME.

If we pour, drop by drop by means of a graduated burette, a solution of chromic acid (1 part of $\text{CrO}_3 + 200$ parts H_2O) into a solution of yellow prussiate treated with sulphuric acid ($2 \cdot 11 \text{FeCy}_6\text{K}_4 + 100\text{H}_2\text{O} + 5\text{H}_2\text{SO}_4$), we observe that at a certain point a drop of the mixture will turn filter-paper impregnated with tincture of guaiacol blue.

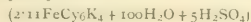
We might think that this colouration is due to an excess of chromic acid, the whole of the ferro-hydrocyanic acid having been transformed into ferri-hydrocyanic acid. In reality this is not the case, and the transformation of the ferro-hydrocyanic acid does not take place integrally. I have, in fact, made the following observations:—

1. Ferri-hydrocyanic acid—



alone gives a blue colour to paper impregnated with tincture of guaiacol.

2. Ferrohydrocyanic acid—



does not colour it.

3. The presence of small quantities of ferro-hydrocyanic acid prevents the ferri-hydrocyanic acid from turning guaiacol paper blue.

As this colouration is the result of oxidation, it must be admitted that the ferri-hydrocyanic acid is hydrolysed, giving ferro-hydrocyanic acid and oxygen. But the inverse reaction takes place, and chemical equilibrium will be represented by the two systems which change one into the other, $\text{Fe}_2\text{Cy}_{12}\text{H}_6 + \text{H}_2\text{O} \rightleftharpoons 2\text{FeCy}_6\text{H}_4 + \text{O}$.

The relative speeds of the two reactions would be known if we could determine the proportionate quantities of the two acids which are in equilibrium, in comparison with the reaction of the paper impregnated with tincture of guaiacol. Ordinary filter-paper will do very well for this purpose.

1. Ordinary filter-paper is coloured blue almost immediately when a drop of ferro-hydrocyanic acid of the above mentioned strength is placed on it. This property is evidently due to defective washing during manufacture after chlorination. The ferro-hydrocyanic acid, which gives prussian blue on oxidation, is oxidised by the paper itself.

2. Ferri-hydrocyanic acid, at the above mentioned strength, makes a yellow stain on this paper; this turns slightly green after a fairly long interval.

3. A mixture of ferro- and ferri-hydrocyanic acids makes a yellow stain on filter-paper, becoming green rapidly, and the more of the former acid there is in the mixture the quicker the green colour appears.

With known volumes of ferro-hydrocyanic acid solution, we note the volumes of chromic acid solution necessary to cause the appearance of the blue colouration on paper impregnated with tincture of guaiacol. Then we continue to add chromic acid, using ordinary filter-paper for the reaction, until a drop of the mixture causes a permanent yellow colouration. The ratio between the two amounts of chromic acid thus measured was found to be constant and equal to 10:1. This figure represents the ratio of the speeds with which the two inverse reactions take place.

Estimation of the Yellow Prussiate.—We can estimate the yellow prussiate by utilising the properties just described above. Its aqueous solution is treated with a suitable amount of sulphuric acid, about 5 per cent, and then with a 5 per cent solution of chromic acid. The blue colouration of the paper impregnated with guaiacol shows that the end of the reaction is approaching. At this moment we substitute ordinary filter-paper, which takes successively a green colouration, becoming more and more yellow.

We stop when the stain remains a pure yellow. With the above mentioned strengths it is necessary to deduct from the number of c.c. of chromic acid a constant volume of 0.25 c.c. added in excess to obtain the persistent yellow colouration.—*Bull. Soc. Chim.*, Series 3, vol., xxix., No. 20.

EXAMINATION OF SOME ANCIENT SAMPLES OF BREAD.

By L. LINDET

THE fragments of bread, carefully collected and preserved by archaeologists, have an appearance and chemical composition which depends on the physical conditions to which they have been exposed. I thought it would be of interest, as I have a certain number of samples in my possession, of which several were collected by Aimé Girard, to examine the whole question.

1. *Bread from Pompeii.* (Sent to A. Girard by Prof. Cannizaro, in the name of the Minister of Education in Italy).—The breads found at Pompeii in 1862 are the best known; they have been described and analysed by de Luca (*Comptes Rendus*, 1863, vol. lvii., p. 473); they have the appearance of a porous carbon in which no trace of any of the elements of bread can be found, and they contain, in the same manner as coke or animal black, a considerable proportion of nitrogen, varying from 2.6 to 2.8 per cent. This nitrogen is not in the form of ammoniacal salts, susceptible of being displaced by magnesia, nor in the form of amines decomposable by soda. It is in the particular form which can be best described as cyanic nitrogen, capable of giving indol, pyridine, or paracyanogen by the action of dry heat; the nitrated molecule exists, in fact, in the last stage of its decomposition. It is evident that this amount of nitrogen remaining in the carbon of a calcined organic substance depends on the temperature to which this substance has been subjected; so that the estimation of the nitrogen gives us some idea of the temperature to which these samples of bread have been exposed. By heating a piece of compact bread, similar to that which would most likely be made at the time, to 350–400° in a closed vessel. I obtained a porous carbon identical in appearance with those samples found at Pompeii, containing 2.81 per cent of nitrogen, while one of the specimens now in my possession contains 2.65 per cent. Geologists agree in stating that the ashes of Vesuvius,

* To estimate this temperature, I placed a specimen of bread, fused at 335° and zinc-fusing at 412° in the closed tin-temperatures furnace.

which overwhelmed Pompeii in the year 79 B.C., were not very hot.

All traces of starch and cellulose have disappeared; hydrolysis does not give any reducing sugary material; however, some ulmic materials remain, capable of giving a small quantity of acetic acid on dry distillation.

The crumbs give the reaction for chlorides very distinctly; it is known that the Romans put salt into their pastry (Pliny, "Farina subigitur priusquam addatur sal," "Hist. Nat." Book XVIII., p. 26).

II. *Bread from Lake Dwellings*.—It is in a similar condition that the specimens of bread from lake dwellings were found, discovered in different lakes after the burning of the dwellings placed therein.

In a sample from Corcellettes in Lake Neuchâtel (the bronze age), I only found a nitrated carbon ($N=2.46$ per cent) enclosed in vegetable *débris*, dredged up from the bottom of the lake. In another sample, less carbonised and of a reddish-brown colour, found in Lake Bourget ($N=4.69$ per cent), I was able distinctly to distinguish the *débris* of grains still existing, and especially fragments of the outer skin of the grain of barley, as well as of grains of starch. Further, barley is the oldest cereal known; four kinds of barley have been found in the districts of Switzerland and the Savoy (De Candolle, "Origin of Cultivated Plants," p. 296).

III. *Bread from Egyptian Tombs*.—Bread intended for the use of the dead, and which was enclosed in their tombs, has been admirably preserved, and is found to-day in the same condition as in which it was enclosed. In Egyptian tombs, we meet sometimes with unleavened bread in the form of flat cakes, and sometimes with leavened bread. Further, the Egyptians were familiar with yeast, since the Hebrews made use of it. The two samples I have had (sent by M. Nachet) were of unleavened bread, and entire, in which I could easily recognise the *débris* of the husk of the barley (outer epidermis, fibrous hypoderm of the grain, cells of proteic acids, radicular hairs). Now we know that the gluten of barley has no elastic properties; barley bread will not rise. The paste contains a quantity of gluten and a quantity of starch, which may be considered as normal. In my two samples I found 11.25 and 11.40 per cent of nitrogenous material ($N=1.80$ and 1.83), and 68.0 and 65.2 per cent of starch. This starch, as in a baked bread, is found in two forms; one part is solubilised in the form of soluble starch and dextrin (20.4 per cent). It is of more importance than in the ordinary cases, because this bread, slightly browned, has evidently been heated to a high temperature, as is proved by the acidity of the crust. The other part is in the form of swelled-up crumb; only a very few grains of starch have remained intact.

I have shown (*Comptes Rendus*, 1902, vol. cxxiv., p. 908) that the temperature might have been estimated from the amount of gelatinisation of the starch, by treating the bread with hydrochloric pepsin (1.5 c.c. of HCl), and there again we observe that the amount of starch dissolved in the dilute acid goes beyond the ordinary limits (21.3 per cent). One of these samples of bread contains 4.5 per cent of ash, in which the presence of chlorides is found. The salt used by the Egyptians was rich in nitrates; these latter can be easily detected in the bread by means of diphenylamine.

IV. *Roman Bread from Aosta*.—In 1856, researches brought to light at Aosta, in a place called La Maria, various Roman objects, among which was found a fragment of bread, representing the quarter of a round loaf 30 or 40 c.m. in diameter. This loaf was entirely transformed, by decay and refilling of the matrix, into a morsel of sandstone consisting of granitic elements (mica and felspar). This pseudomorph has an interest that is not entirely geological. I have found, in fact, several grains of starch embedded in the mineral matter, and this leaves no doubt as to the nature of the fragment discovered at Aosta. These grains of starch, not broken down by cooking, have resisted the action of the water which

brought the granitic elements; the grains of corn which were in the mucous condition have been destroyed, as was also the gluten. Microscopic examination leads me to the conclusion that these grains of starch are from wheat.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 23.

PROCEEDINGS OF SOCIETIES.

THE FARADAY SOCIETY.

Ordinary Meeting, April 13th, 1904.

The meeting was held at the Institution of Electrical Engineers, Mr. J. SWINBURNE, Vice-President, in the Chair.

Mr. ARTHUR J. HIORNS read an abstract of his paper on "*Alloys of Copper and Arsenic*," illustrating his remarks by a series of interesting and beautiful lantern slides.

The object of the author's investigations was to ascertain the exact relation between copper and arsenic in binary alloys, and the limit of proportion of arsenic that can be retained in copper in the cold solid state.

The addition of arsenic lowers the melting-point of copper uniformly down to about 14 per cent, when a steep fall in the freezing-point curve occurs, reaching its lowest point at 68.5° C. This alloy contains 19.2 per cent of arsenic, which corresponds to the formula Cu_3As_2 . The alloy with 22 per cent of arsenic freezes at 708°, and the temperature gradually rises until the alloy with 28.34 is reached at 747°. This is the compound Cu_2As_3 . At 810° another chemical compound freezes, having the chemical formula Cu_2As_2 ; it contains 32.2 per cent of arsenic. Beyond this point the temperature gradually falls again to a minimum at the alloy, with about 35 per cent of arsenic. The curve then rises to another summit at 740°, forming the compound Cu_2As , with 37.24 per cent of arsenic. From this position the curve descends to 702° with the alloy containing 41 per cent of arsenic; this is nearly the practical limit of the direct combination of copper and arsenic.

The top surfaces of many of the alloys were photographed. The types of pattern visible on the etched surface depend upon the position of the freezing-point on the curve. For alloys whose freezing-point is on or near the summit of a curve, the whole of the section is composed of one substance, generally made up of crystal grains having fine boundaries. When by addition of copper or arsenic a summit of a curve is left, the lines between the crystal grains widen and become filled with a network of matter differing from that of the crystals, and generally showing a more or less striated appearance, so characteristic of eutectics. As the bottom of a curve leading from a summit is reached, the eutectic occupies the whole surface. It is noticeable that the alloy of minimum fusion of copper-arsenic alloys has an extremely fine striated structure. Any deviation in composition from the eutectic proportion causes the breaking up of this striated pattern, and grains of one of the constituents appear in the eutectic matrix.

A microscopic examination was also made of polished sections of the various alloys. These when viewed in daylight are all copper-coloured in those with little arsenic, and gradually get paler as the arsenic is increased. When the alloy with 19.2 per cent is reached, the surface appears of a pale blue colour, and this is continued up to the compound Cu_3As_2 , containing 28.34 per cent, which is of a deeper blue colour. The alloys between 19.2 and 28.3 per cent have a paler blue tint, because the blue constituent is associated with a constituent richer in copper, forming a eutectic mixture. The alloy with 30.0 per cent is of a light purple colour, and when the compound Cu_2As_3 is reached, containing 32.2 per cent, a full reddish purple is obtained. This purple colour maintains up to the limit of

these experiments with 45 per cent of arsenic, but gets gradually paler.

The paper concludes with a detailed description of the various alloys, fully illustrated by excellent photomicrographs.

Mr. SWINBURNE, referring to the melting-point of arsenic, which the author thought could only be obtained by experiments made under great pressure, observed that the effect of pressure on the melting-point of solids is very small, and that probably at ordinary pressures the melting-point of arsenic was very close to its volatilising point.

Dr. PERKIN hoped that the author would supplement his researches by making conductivity measurements of the series of alloys.

Dr. C. H. DESCH made some interesting comparisons between the results obtained by the author and those published by other investigators, in the case of the analogous series of copper-antimony alloys.

Mr. E. G. P. BOUSFIELD contributed a paper on "*Experiments with a New Primary Cell.*"

The cell consists of an inner porous pot containing nitric acid and a carbon pole, and an outer vessel containing sodium hydrate solution and a metal pole, preferably zinc, *i.e.*, a solution of from 12 per cent to 15 per cent, using solutions of maximum conductivity with zinc and carbon poles on open circuit, an E.M.F. of 2.6 volts may be obtained. Not only does the cell possess this comparatively high E.M.F., but it may be short-circuited far longer than most cells before it runs down. A cell short-circuited through a total resistance of 0.61 ohms gave a current of 4.18 amperes, which fell to 2.61 in an hour, 2.38 in two and a quarter hours, and 1.75 in six hours. A smaller cell gave a fairly constant current of about 0.8 ampere for twenty or twenty-five hours. Discharge curves are given in the paper.

Acids other than nitrate were experimented with. Some of them gave higher E.M.F.'s than nitric acid, but no other acid possessed the same "lasting powers." The effect of using various metals instead of zinc was also tried; some of these gave higher E.M.F.'s than the zinc, but the high readings were quite transitory. Using two carbon poles the E.M.F. was about 1.35 volts. The cell is then similar to Becquerel's platinum cell, in which the plates are immersed in acid and caustic potash respectively.

Mr. W. R. COOPER referred to the disadvantages of both nitric acid and caustic soda as electrolytes. The high E.M.F. of the cell was only apparent, because it rapidly fell to a working value of 1.8 or 1.9. He would like to have seen comparative tests made, say with a bichromate cell.

Mr. J. SWINBURNE mentioned a suggestion made by Dr. Swan, that the cell would be improved if it were converted into a three-fluid cell, with a neutral electrolyte (*e.g.*, NaNO_3) in the mid compartment.

Mr. BOUSFIELD also contributed a "*Note on Determining Accurately the Percentage of Ozone in Gases not Dissociated by Moderate Heat.*"

Difficulty was found in determining accurately the quantities of ozone formed in different electrolytic reactions. The potassium iodide test is sufficiently accurate for most purposes, but for very accurate work it is not satisfactory, as an error of 5 per cent or more is often obtained with a slightly alkaline solution, and an error of as much as 1 or 2 per cent with an acid solution. Estimating the ozone by weight, using glass globes for that purpose, was also found to be somewhat uncertain, due to the condensation of moisture on the glass. The method recommended by the author is a measurement by volume. A certain quantity of gas containing ozone is measured. This gas is then passed over some substance, such as heated platinised asbestos, which is capable of converting ozone into ordinary oxygen. On again measuring the gases, an increase of volume due to the breaking down of " O_3 " molecules into " O_2 " molecules is

found. From this increase of volume the quantity and percentage of ozone originally present is readily calculated. A description of the simple apparatus required for the measurements is given in the paper.

NOTICES OF BOOKS.

Electrolytic Preparations. By Dr. KARL ELBS. Translated by R. S. HUTTON, M.Sc. London: Edward Arnold. 1903. Pp. 100.

THIS volume consists principally of exercises for use in the laboratory by chemists and electro-chemists, a branch of the subject which has not hitherto been very fully dealt with in text-books. It is assumed that those who intend to make use of these exercises are already familiar with practical chemistry and physics, and especially the laws governing electric currents.

The first sixteen pages are on general matters connected with the source of current, connections, resistances, measuring, and other apparatus to be used.

Part II., or the "special" part, fills the rest of the book, and is divided into various sections and sub-divisions.

First in order come examples from inorganic chemistry with insoluble anodes, then others with soluble anodes.

The section on organic chemistry includes the electrolysis of organic acids, electro-chemical methods of reduction, and electro-chemical oxidation methods.

A careful study of this volume will put into the hands of the chemist another means for the preparation of a large number of chemical substances, and will familiarise him with the growing subject of electrolytic analysis.

Aids to Chemistry. By T. A. HENRY, D.Sc.(Lond.), F.C.S., &c. Eighth Edition. London: Baillière, Tindall, and Cox. 1903. Pp. 316.

In this edition of "*Aids to Chemistry*" it has been found necessary to entirely re-write it, and to assist the medical and pharmaceutical student as much as possible, the theoretical portions of the book have been treated on broad lines, and, as far as possible, in immediate conjunction with experimentally ascertained facts serving to illustrate them.

The first portion of the book deals with inorganic chemistry, the properties and characteristics of the metals and their salts, while the latter part is on organic chemistry, or the chemistry of the carbon compounds. The whole is well arranged and adapted for the use of students.

The Phase Rule and its Applications. By ALEX. FINDLAY, M.A., Ph.D., D.Sc. London, New York, and Bombay: Longmans, Green, & Co. 1904.

THE first of the proposed series of manuals dealing with different branches of physical chemistry is devoted to the study of the principles underlying the phase rule of Willard Gibbs. The treatment of the subject is quite unmathematical, and, comparatively speaking, elementary. The least satisfactory part of the book is certainly that which treats of the general exposition of the rule, which requires very close attention throughout, and would probably be in places rather beyond the comprehension of the young student. The application of the general principles to the study of various examples is, however, in all respects excellent; as, for example, in the chapter giving a general summary of the various relationships discovered on applying the rule to systems of one component. Under the heading of two components are studied the phenomena of dissociation and solution; the treatment of three and four component systems, though very lucid, has been necessarily somewhat restricted owing to the great complexity of these systems.

With the volume is bound the "General Introduction to the Study of Physical Chemistry," written by Sir William Ramsay, the editor of the series.

CORRESPONDENCE.

THERMO-CHEMISTRY OF ELECTROLYTIC DISSOCIATION.

To the Editor of the *Chemical News*.

SIR,—It is with pleasure I have read Mr. P. J. Beveridge's letter (*CHEMICAL NEWS*, lxxxix., p. 82), in which he has taken exception to the calculation used by Mr. Richards (*CHEMICAL NEWS*, lxxxix., p. 31, 37) in support of his theory of solution. Mr. Beveridge has clearly pointed out the remarkable coincidence that the concentration in the single example cited from the work of Thomsen is the only one which, applying a calculation for outer work as Mr. Richards has done, gives an agreement with the observed heat of neutralisation, 13,740 calories.

Mr. Richards's paper, read at general meeting of the American Electro-chemical Society, Niagara Falls, Sept., 1903, happened to be brought into the discussion at the meeting of the New York section of that society, January 26th, 1904. As this numerical agreement of Prof. Richards was mentioned, the writer called the attention of the Section to the fact that he, in calculating this external work, had been unable to obtain this agreement even in the example given by Richards. And that this seemed due to an erroneous application by Prof. Richards of the ordinary gas laws.

The example quoted gives the reaction of two molecules, NaOH and 2HCl, in 800 water, with liberation of 27,480 calories heat of neutralisation, or 13,740 for each molecule. 800 H₂O having a volume of 14.4 litres, and the osmotic pressure of the OH' and H' being, according to Richards, 6.19 atmospheres, the volume energy is 6.19 × 14.4 litre-atmospheres.

The thermodynamic constant, 2T, is the value in calories for RT in the equation $p\bar{v} = RT$ when $p = 1$ atmosphere, $\bar{v} = 22.4$ litres (volume of 1 molecule gas at 0°C. at atmospheric pressure). Nevertheless, Prof. Richards in his example, having a volume smaller than the normal and a pressure greater, took into account only the ratio of the pressure to the normal pressure, and not, as he should have, the ratio of the product of the pressure and volume to the product of the normal pressure and volume, which would give in the following form of calculation:—

$$\frac{6.19 \times 14.4}{1 \times 22.4} \times 2T = 4 \times 2T = 8T \text{ calories.}$$

That as Prof. Richards distinctly states this is the external work of evaporating two molecules H₂O, and as the 10,110 calories latent heat to which it is added is just as distinctly stated by him to be for one molecule H₂O ("18 parts"), the above external work should be divided by 2, which gives 2(2T) cal. = 164 calories, 10,110 + 164 = 11,274 calories. The difference between which and 13,740 is 2466 calories, and not 40 as he has obtained. The very form of the gas law, $p\bar{v} = RT$, teaches us that since the product of pressure and volume for any given temperature is constant, the external work necessary to form a molecule of gas is a constant quantity independent of the pressure under which the gas is formed. The work then to form one molecule any gas, no matter what the pressure is, and can only be 2T calories.

On the other hand, for substances in solution which dissociate, and therefore which show an osmotic pressure greater than they would were they gaseous and occupying similar volume, the van't Hoff equation, $p\bar{v} = iRT$, holds, and since if in the above aqueous solution we assume complete dissociation (as Mr. Richards must have done to obtain calculated osmotic pressure of 6.19 atmospheres), $i = 2$. The work needed to force one molecule

H₂O into the two ions, OH' and H', is given directly by $iRT = 2 \times 2T = 4T$ calories. So Richards's calculation is unnecessary, as it is merely a reversal of that made by him in obtaining the osmotic pressure in the first place.

Thus, then, 10,110 + 164 = 11,074 calories out of 18,740 is the utmost that Prof. Richards's theory can account for on a basis of mere physical change, and as Prof. Richards's whole theory is to the fact that in diluted solution the elements are in an ideal combined condition, and that therefore no further chemical combination can occur, it is hardly necessary to point out that not only has Prof. Richards's failed in substantiating his theory, but that the figures given by him are rather a strong argument that the converse is true.

In the second example, since the heat for the formation of the gas is independent of the pressure, the calculation of $(619 - 1) \times 2T = 3021$ calories is without meaning, and that therefore he has proved nothing, or rather proven that the "ionised water molecule" is not identical with the gaseous state of water-vapour at the same pressure.

The following result *can*, however, be obtained from the values for H' and OH' given by Richards from his tables.

Since $\frac{1}{2}(H_2) = H' - 900$ calories, and $\frac{1}{2}(O_2) + \frac{1}{2}(H_2) = OH' + 56,100$ calories, and H' and OH' cannot continue their separate existences in the same solution, but react with further liberation of 13,740 calories, we have the equations $\frac{1}{2}(H_2) + \frac{1}{2}(O_2) + \frac{1}{2}(H_2) = H' + OH' + 55,200$ cal., $H' + OH' = H_2O + 13,740$ cal., then $(H_2) + \frac{1}{2}(O_2) = H_2O + 55,200 + 13,740 = H_2O + 68,940$ calories.

This is for the formation of 1 molecule liquid water in diluted solution. The evaporation of this 1 molecule H₂O will require 10,692 calories, leaving 58,252 calories, which number does agree with Regnault's 58,100 calories for the direct formation of water-vapour from oxygen and hydrogen gases. However, in this we have taken into account 13,740 calories chemical action which does occur and which Richards has ignored.

The elaborate tables of thermo-chemical constants which Richards has prepared in no wise help his theory, since they are but an elaboration of, and another name for, the heats of ionisation, a short table of which was published by Ostwald in 1893 (*Zeit. für Physik. Chem.*, xl., p. 501). These as far as they are given agree with Richards, but differ from Ostwald's re-calculated values given by him in his "Grundriss der Allgemeinen Chemie," p. 281.—I am, &c.,

H. A. JACKSON.

March 15th, 1904

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 12, March 21, 1904.

Density of Fluorine.—Henri Moissan.—After the discovery that fluorine, when absolutely free from hydrofluoric acid, does not act on dry clean glass, a series of new determinations of the density of fluorine are made by filling a glass bulb with the gas and weighing. The author describes the various precautions necessary for these determinations. His four experiments give respectively the numbers 1.298, 1.319, 1.313, and 1.312; the mean is 1.31. The theoretical density should be $0.06927 \times 19.05 = 1.319$, taking 19.05 as the atomic weight of fluorine. These two numbers are almost identical, and 1.31 can therefore be admitted as the experimental density of fluorine.

Colloidal Solutions. Application of the Rule of Phases to an Investigation of the Precipitation of Colloids.—Victor Henri and André Mayer.—The rule of phases, when applied to colloidal solutions in the same manner as to all normal solutions, allows of an examina-

tation and systematic classification of the conditions of precipitation of the whole series of colloids.

Transformation of Oxides and Oxygen Salts into Chlorides.—C. Matignon and F. Bourion.—The action of sulphur chloride and chlorine allows of the transformation of oxides and oxygen salts into anhydrous chlorides. This transformation can in many cases be advantageously employed for analytical work.

Silver and Lead Salts of Monoalcoylphosphoric Acids.—J. Ca-valier.—Monoethyl- and monoallyl-phosphoric acids behave towards silver and lead salts in an analogous manner to phosphoric acid. The soluble mono-metallic salts, neutral to methyl-orange, give, on addition of lead or silver nitrate, a precipitate of bi-metallic salt, and the liquor becomes acid to methyl-orange. The mono-metallic salts of lead and silver can only be formed in a very strongly acid medium.

Certain Amino-alcohols of Tertiary Alcoholic

Function of the Type $\text{R}-\text{COH}-\text{CH}_3$
 $\text{CH}_2\text{N}-\text{CH}_3$ — E.

Fourneau.—The author obtains the amino-alcohols of tertiary alcoholic function by heating the chlorohydrines with a little more than two molecules of a tertiary or secondary amine dissolved in alcohol. These are isolated by driving out a portion of the solvent by boiling; this contains the excess of amine. He then separates the base by dilute hydrochloric acid. This base is freed again by caustic soda, after carefully washing the acid solution with benzene. The base extracted by ether is distilled *in vacuo*, and the yield is 80 per cent.

MISCELLANEOUS.

Research on Dicalcic Phosphate. Artificial Production of Brushite and Monetite.—A. de Schulten.—The hydrated dicalcic phosphate, $\text{PO}_4\text{CaH} + 2\text{H}_2\text{O}$ (brushite), is easily obtained in microscopic crystals when we leave the salt precipitated from CaCl_2 by $\text{PO}_4\text{Na}_2\text{H}$ in contact with its mother-liquor. The author has obtained these crystals of a measurable size by dissolving PO_4CaH in the cold, up to saturation-point, in 25 per cent acetic acid, then letting the filtrate evaporate slowly in the cold. Wash with glacial acetic acid, alcohol, and ether. Clinorhombic tables are formed, flattened along g_1 with $ph_2a_3(d_1b_1g_1)$, isomorphous with pharmacolite, $\text{AsO}_4\text{CaH} + 2\text{H}_2\text{O}$: $D = 2.317$. The author has attempted to obtain the lower hydrates at a higher temperature (meta-brushite which should be $1.5\text{H}_2\text{O}$ is very doubtful). Starting at 50° , and especially at about 100° , the brushite is transformed into the anhydrous salt, PO_4CaH (monetite). A solution of CO_2Ca in PO_4H_3 , filtered and heated to 155° (and even to 260°), gives anorthic crystals, generally flattened along h_1 , with the faces $pg_1mo_2c_3(d_1b_1h_1)$.—*Bull. Soc. Min.*, vol. xxvi, p. 11.

The Use of Hydroxylamine and Hydrazine in Qualitative Analysis.—E. Kiroevenagel and E. Eber.—The salts of hydroxylamine or of hydrazine may be used for the separation of the metals precipitated by sulphuretted hydrogen. The principle of the method is as follows:—The precipitated sulphides are well washed and dissolved in aqua regia, the excess of acid is evaporated off, and the residue taken up with water, and precipitated by a mixture of NaOH and a solution of sulphate of hydrazine or hydrochlorate of hydroxylamine; after boiling, allow to cool, and filter. The precipitate (P_1) contains Hg, Cu, Cd(OH) $_2$, Bi(OH) $_3$, and traces of Ag; the filtrate (F_1) contains AsO_4Na_3 , SbO_4Na_3 , Na_2SbO_3 , Pb(ONa) $_2$, and traces of bismuth. The precipitate (P_1) is dissolved in nitric acid, and the solution, on the addition of ammonia, throws down Bi(OH) $_3$; the filtrate is treated with hydrochlorate of hydroxylamine, which precipitates the Hg; if copper is present the solution is decolorised while main-

taining the copper in solution; it is precipitated by means of sulphocyanide; nothing remains in solution but the cadmium which is precipitated by sulphuretted hydrogen. The filtrate (F_1) is saturated with H_2S , the lead separates out, there remain the tin, arsenic, and antimony. On the addition of dilute sulphuric acid, the sulphides of these metals are deposited, and can be separated in the usual manner.—*Berichte*, vol. xxxv, p. 3055.

The Formation of Peroxides in the case of Iron.—M. Manchot.—The principle of these experiments is as follows:—A ferrous salt is submitted to the action of an oxidising agent simultaneously with an acceptor. The acceptor is a body whose oxidation, very slow if it was the only reducing agent, is made very rapid by the simultaneous presence of the ferrous reducing agent. Under these conditions we observe both the oxidation of the ferrous salt and of the acceptor. If the latter is in excess, the oxygen that it uses up, added to that which has changed the ferrous salt to the state of ferric salt, gives the total oxygen taking part in the reaction, and furnishes the formula of the transitory peroxide which is formed. This oxide comes directly before the ferric degree. Using chromic acid as the oxidiser and hydriodic acid as the acceptor, we find that the primary oxide is Fe_2O_3 . The same is the case with permanganate and tartaric acid, and with H_2O_2 . Oxygen gas gives FeO_2 as the primary oxide. Hypochlorous acid gives FeO_3 . The ferric salts themselves are distinctly capable of peroxidation. Thus their presence accelerates the decoloration of indigo by oxidising agents (less decidedly, it is true, than with the ferrous salts). The oxidising action of dilute peroxide of hydrogen is prevented by the presence of acids. The oxides FeO_2 and Fe_2O_3 have not been isolated, but their existence as primary oxides does not seem the less proved by these experiments.—*Liebig's Ann. Ch.*, vol. cccxxv, p. 105.

MEETINGS FOR THE WEEK.

- MONDAY, 25th.—Society of Arts, 4.30. (Cantor lectures), "The Majolica and Glazed Earthenware of Tuscany," by Prof. R. Langton Douglas, M.A.
TUESDAY, 26th.—Royal Institution, 5. "The Transformations of Animals," by Prof. L. C. Miall, F.R.S.
WEDNESDAY, 27th.—Society of Arts, 8. "The Need of Duty-free Spirit," by Thomas Tyler.
THURSDAY 28th.—Royal Institution, 5. "Dissociation," by Prof Dewar, F.R.S., &c.
FRIDAY, 29th.—Royal Institution, 9. "Westminster Abbey in the Early Part of the Seventeenth Century," by The Very Rev. J. A. Robinson, D.D.
SATURDAY, 30th.—Royal Institution, 3. "Jewellery," by Cyril Davenport, F.S.A.

BACTERIOLOGY.

KING'S COLLEGE, LONDON.

Professor HEWLETT, M.D., D.P.H.
H. S. WILSON, M.B., D.P.H.

COURSES OF INSTRUCTION are given in GENERAL BACTERIOLOGY, the BACTERIOLOGY OF FERMENTATION, and for the Examinations of the Institute of Chemistry. The Laboratories re-open on May 2nd, but Students may enter at any time. Vacation Course, AUGUST 3rd to 10th. For Syllabus and further information, apply to the SECRETARY or to Professor HEWLETT.

NOTICE.

Mdme. CURIE'S Thesis

ON

RADIO-ACTIVE SUBSTANCES.

REPRINTED from the CHEMICAL NEWS.

The First Edition being exhausted, a SECOND EDITION is in course of preparation and will be ready shortly.

Price 2s. net (post free 2s. 1d.)

10, NEWCASTLE ST., FARRINGTON ST., E.C.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2318.

PHYSICAL CONSTANTS AT LOW TEMPERATURES.*

I. THE DENSITIES OF SOLID OXYGEN, NITROGEN, HYDROGEN, &c.

By Prof. JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

1. The following experiments on the solid densities of oxygen, nitrogen, and hydrogen were carried out as part of a former investigation dealing with gaseous densities at low temperatures ("The Specific Volumes of Oxygen and Nitrogen Vapour at the Boiling-point of Oxygen," *Roy. Soc. Proc.*, vol. lxxx.).

The method adopted was to measure the volumes of the gases sucked into a cooled space of known capacity, when the temperature was such as in the first place to induce liquefaction, and finally solidification. For such experiments to be successful the rate of liquefaction and the cooling must be under thorough control, otherwise the cooled space may not get completely filled with solid. Further, the volume of gas condensed ought to be as large as possible, in any case about 20 litres, in order to diminish errors inseparable from the mode of manipulation. The inertia of the bell-jars of the large gas-holders causes some variation in the pressure; and errors of their calibration, and want of uniformity of temperature in the mass of gas, are all important factors. As my object was to ascertain experimentally the limiting density in the solid state, the elimination of these variations was not so important as it would have been for the study of fluid density.

The dry purified gas was contained in a gas-holder connected by a pipe with a glass bulb of 20 or 30 c.c. capacity, sealed to a narrow tube some 10 c.m. long with a glass stop-cock at the end. The glass bulb was immersed in liquid oxygen, nitrogen, or hydrogen contained in a vacuum-jacketed vessel, with arrangements for lowering the temperature of the liquids by exhaustion. The narrow tube just above the glass bulb had a mark engraved upon it, and the volume up to this point, which is to be filled with liquid or solid after cooling, was antecedently carefully calibrated. The glass stop-cock on the projecting part of the glass tube outside the vacuum vessel enabled the rate of the gas supply to be under complete control. The real difficulties were those of manipulation.

The temperatures employed were the boiling-point of oxygen, 90°; the boiling-point of nitrogen, 77°; the melting-point of nitrogen, 62°; the boiling-point of hydrogen, 20°; hydrogen boiling under 76 m.m. of pressure taken as 14°; and hydrogen (solid) under 10 m.m. of pressure taken as 13°.

Allowance for the contraction of the bulb was made by taking 0.0000250 as the coefficient of contraction (cubical) of the glass. It is possible that in going to very low temperatures (below -200° C.), this coefficient ought to be less, such as 0.0000225. An estimate made of the difference between the two would come within the range of errors, consequently the former value which was adopted in the earlier investigations was retained.

The weight of 1 litre of oxygen at 0° C. under 760 m.m. pressure was taken as 1.430 grms., of nitrogen as 1.2564 grms., and of hydrogen as 0.0899 grm.

The observations and results are given in the following tables:—

TABLE I.—Oxygen.

No.	Description	T°	V	T	ρ m.m.	d
1.	At b.p. of O ..	-182.5	10.631	14.1	758.5	1.1181
2.	At b.p. of N ..	-195.5	20.536	14.1	758.5	1.1700
3.	At m.p. of N ..	-210.5	21.743	14.55	758.5	1.2486
4.	At b.p. of H ..	-252.5	25.003	14.6	758.5	1.2566
			(solid)			

Where T° = the temperature Centigrade of the condensed gas in the flask at the time of observation.

V = volume of gas in litres at temperature T° C. and pressure ρ m.m.

d = density of the condensed gas at T° C.

The volume of the flask at 15° C. was 23.9212 c.c.

Coefficient of expansion of glass, taken as 0.0000250.

Weight of 1 litre of oxygen at 0° C. and 760 m.m., taken as 1.430 grms.

TABLE II.—Nitrogen.

No.	Description	T°	V	T	ρ m.m.	d
1.	At b.p. of N ..	-195.5	18.192	16.1	747	0.8042
2.	At m.p. of N ..	-210.5	19.592	15.95	747	0.8792
3.	At b.p. of H ..	-252.5	18.911	14.65	761	1.0265
			(solid)			

The same notation is used as in Table I.

The volume of the flask at 14° C. was 22.1454 c.c.

Coefficient of expansion of glass, 0.0000250.

Weight of 1 litre of nitrogen at 0° C. and 760 m.m., 1.2564.

TABLE III.—Hydrogen.

No.	Description	T°	V	T	ρ m.m.	d
1.	At b.p. of H ..	-252.5	18.051	14.6	760	0.07004
2.	Under 76 m.m.	-258.29	19.447	14.6	760	0.07544
3.	H under 10 m.m.	-259.9	19.597	14.3	762	0.0763
			(solid)			

The same notation is used as in Table I.

The volume of the flask at 14° C. was 22.1454 c.c.

Coefficient of expansion of glass, 0.0000250.

Weight of 1 litre of hydrogen at 0° C. and 760 m.m., taken as 0.0899.

2. It is of advantage to estimate the effects of an error, or of any reading that may have been taken roughly. Taking the notation already employed, and putting w for the weight of 1 litre of the gas at 0° C. and 760 m.m., then the weight of gas used is—

$$W = \frac{V \rho 273}{760 (273 + T)} w$$

and if V_0 be the volume of the flask up to the mark at some ordinary temperature T° C., and V' its volume at T° the temperature Centigrade of the observations, then—

$$V' = V_0 \frac{1 + \beta T'}{1 + \beta T_0}$$

where β is the cubical coefficient of expansion of the glass. Hence, the density of the substance at the time of observation is—

$$d = \frac{W}{V} = \frac{V \rho 273 w}{760 (273 + T)} \times \frac{1 + \beta T_0}{V_0 (1 + \beta T')}$$

or, with sufficient accuracy for our investigation,—

$$d = \frac{273 w}{760 V_0} \times \frac{\rho (1 + \beta T_0 - T')}{273 + T} \quad (1)$$

An important error might be expected to arise from an inaccurate knowledge of T', the temperature of the cooled gas. An alteration of a degree in the value of T' would alter the value of d by—

$$- \frac{273 w}{760 V_0} \times \frac{\rho}{273 + T} \beta$$

or very approximately, a rise of a degree in the estimate of T' above its true value would diminish d by βd —in the present case by 1/40000 part.

* A Paper read before the Royal Society, March 17, 1904.

Similarly an error of a degree in the estimate of the temperature T_0 , at which the volume of the flask was measured, would have the like small effect, but in the opposite direction.

On the other hand, errors in the measurements of either V or V_0 or of p or T would give directly proportional errors in the value of d . The values of T were easily read to one-tenth of a degree, so that an error in this quantity would have an effect less than $1/3000$ on the value of d . Similarly the pressure was read to $\frac{1}{2}$ m.m., leaving an error of less than $1/1500$ on the density. The volume V showed a tendency to error in the earlier portion of each group of experiments, but this was eliminated as the experiments progressed and especially where the results were more important, namely, in the region of the solidified gases. The greatest care was taken to insure that the whole volume of the bulb was occupied by the solid. The gas was allowed to enter in successive portions, each of which was liquefied and solidified previous to any further admission, so as to insure the absence of any vacua due to contraction.

3. The results for oxygen seem low, the boiling-point density being 1.118 , whereas former results gave 1.138 . On plotting the densities as ordinates to the temperatures as abscissæ the observations lie very closely on a straight line which (by least squares), is—

$$d = 1.5154 - 0.004120t \quad (2),$$

t being absolute temperature.

Such a line as (2) must in any case be only a chord of the curve of liquid densities, and the nearer two observations are to the absolute zero, the more nearly will the chord joining them partake of the nature of a tangent to this curve at the absolute zero. Now, at so low a temperature as 20.5° for oxygen we may consider its gaseous density to be practically negligible. Hence one point on Matthias's rectilinear diameter for oxygen will be, at 20.5° , a density equal to 0.7128 , the half of that given in No. 4, Table I. In former papers I found the density of liquid oxygen at its boiling-point to be 1.138 , and of gaseous oxygen at the same point to be 0.00440 ; half the sum of these is 0.5712 , which gives another point on Matthias's diameter at 90.5° . Thus Matthias's diameter for oxygen is—

$$d = 0.7543 - 0.002023t \quad (3),$$

and taking the critical temperature as 155° absolute we get the critical density to be 0.4407 , agreeing notably with the usually accepted value 0.44 . The inference from this is that the density of solid oxygen at the boiling-point of hydrogen is 1.4256 .

The results for nitrogen, taken at three temperatures, do not warrant the deduction of a linear relation between d and t , especially as on plotting the observations, the concavity of the liquid density curve, though slight, is quite apparent. However, there are two observations at temperatures so low that the corresponding gaseous densities may be neglected, thus enabling us to construct a Matthias diameter. At the boiling-point of hydrogen, the ordinate of the Matthias line is therefore very nearly $\frac{1}{2}$ (1.0265) = 0.5133 ; similarly at the melting-point of nitrogen the ordinate is $\frac{1}{2}$ (0.8792) = 0.4396 . Hence the Matthias diameter is—

$$d = 0.5492 - 0.00175t \quad (4),$$

which for the critical temperature 127° gives the critical density as 0.3269 . This agrees very well with the value deduced by Matthias (*Mém. Soc. Roy. des Sci. de Liège*, 3rd Series, 1899) from Wroblewski's liquid densities, namely 0.333 , though it is somewhat higher than the value 0.299 which he deduced from the theory of corresponding states ("Le Point Critique des Corps Purs," p. 176).

Only three observations have been obtained for hydrogen which again lie nearly on a straight line, but nevertheless present a very slight concavity to the axis of temperature. If we treat the two lowest densities as we have done with nitrogen, we get for the Matthias diameter, the line—

$$d = 0.04136 - 0.000247t \quad (5),$$

whence the annexed table of critical densities according to the—

t_c	d_c
28°	0.03444
29	0.03420
30	0.03395
31	0.03370
32	0.03346
33	0.03321
34	0.03296

temperatures chosen for the critical temperatures. Berthelot gives an estimate for the critical density as 0.033 , and quotes Wroblewski's critical temperature as 33° , two results closely in accord with the numbers in this table. We are, therefore, justified in considering these hydrogen densities as very closely in agreement with facts, the density at the boiling-point coinciding nearly with my former determinations.

4. Assuming that vapour densities at very low temperatures may be neglected in comparison with corresponding liquid densities, the Matthias diameter enables us to approximate to the molecular volumes of the condensed gases at the absolute zero. For if $d' = a - bt$ be the equation of Matthias's diameter, then $d = 2a - bt$ is very approximately the tangent of the liquid density curve near the absolute zero, and therefore $1/2a$ is the specific volume at absolute zero.

Hence from the above equations for Matthias's diameter, if V_0 is the molecular volume at absolute zero, we have $V_0 = 21.21$ for oxygen, $V_0 = 25.49$ for nitrogen, and $V_0 = 24.18$ for hydrogen. The oxygen and nitrogen molecular volumes at absolute zero probably err by defect; but the hydrogen result must be taken as very near the true value.

We may compare these values with the results of theoretical investigation. Guldberg gives for the molecular volume at zero of oxygen 21.5 , and of nitrogen 23.6 (*Zeit. f. Phys. Chem.*, 1895, vol. xvi., p. 7); and Berthelot's values for the same gases respectively are 20.8 and 25.0 (*Comptes Rendus*, March, 1900). From Baly and Donnan's (*Journ. Chem. Soc.*, July, 1902, pp. 911–914) equations for oxygen, nitrogen, carbonic oxide, and argon, deduced from observations within the range of temperature 60° – 90° absolute, we find the following values for the molecular volumes at absolute zero:—oxygen 20.30 ; nitrogen 24.04 ; carbonic oxide 24.54 ; argon 20.34 .

Again, the Waterston-Avenarius formula connecting temperature and fluid volume, namely,—

$$v = c - d \log (A - t) \quad (6),$$

where A is the critical temperature, gives the following equations from Baly and Donnan's results,

Oxygen	$v = 1.9305 - 0.5838 \log (154 - t),$ $V_0 = 20.90, \quad c/d = 3.3.$
Nitrogen	$v = 2.5059 - 0.7868 \log (127 - t),$ $V_0 = 25.80, \quad c/d = 3.27.$
Carbonic oxide	$v = 2.6181 - 0.7948 \log (133 - t),$ $V_0 = 26.04, \quad c/d = 3.29.$
Argon	$v = 1.6331 - 0.5026 \log (155 - t),$ $V_0 = 21.30, \quad c/d = 3.70.$

This same formula has been adopted by Mallet and Friederich (*Arch. Sci. Phys., et Nat.*, July, 1902), subject to the modification that A is a unique temperature to be determined for each substance from experiment. On applying it to twenty-five substances, studied by Sydney Young, they find that A is somewhat higher than the critical temperature, and that c/d is always very nearly equal to 3.78 . Baly and Donnan's observations give rise to these Waterston-Mallet equations:—

Oxygen	$v = 3.88413 - 1.3604 \log (253 - t),$ $V_0 = 19.68, \quad c/d = 2.86.$
Nitrogen	$v = 3.1563 - 1.0560 \log (143.67 - t),$ $V_0 = 24.58, \quad c/d = 2.99.$
Carbonic oxide	$v = 4.60090 - 1.64207 \log (191.1 - t),$ $V_0 = 23.94, \quad c/d = 2.80.$
Argon	$v = 0.98285 - 0.19263 \log (112.4 - t),$ $V_0 = 23.52, \quad c/d = 5.10.$

With assumed values for A, in the neighbourhood of the range of temperature in which we look for the critical temperature, two Waterston-Mallet formulae were constructed for hydrogen based on the data of Table III., namely:—

$$t = 23.22 - 7.530 \log t + 0.5 \quad \text{or} \quad V_0 = 22.90,$$

$$t = 20.84 - 0.592 \log t + 1.5 \quad \text{or} \quad V_0 = 22.62.$$

Assuming that for liquids Van der Waals's equation may be written —

$$\frac{Rt}{v-b} - \frac{a}{v^2} \dots \dots \dots (7).$$

an assumption which has been employed by G. N. Lewis (*Ann. Acad. Arts and Sci.*, 1900, vol. xxxv, pp. 1-27) and others, the results of Table III. give for hydrogen, with this equation, $b = 11.56$, and hence $V_0 = 23.12$.

For comparison these values may be arranged in tabular form thus:—

	O	N.	H	CO	Arg
Present experiments ..	21.21	23.49	24.18	—	—
Guldberg	21.50	23.0	—	—	—
Berthelot	20.78	25.0	—	—	—
Baly, Linear	20.30	24.04	—	24.54	20.34
Baly, Waterston ..	20.90	25.80	—	20.04	21.30
Baly, Waterston-Mallet ..	19.68	24.58	—	23.94	23.52
Waterston-Mallet, for H ..	—	—	22.90	—	—
Waterston-Mallet, for H ..	—	—	22.62	—	—
Lewis	—	—	23.12	—	—

The two Waterston-Mallet results for hydrogen are of importance as showing that even great variations in the value of A affect but little the zero molecular volume. It is further to be remarked that the hydrogen results claim precedence over the others because they have been obtained from observations extending down to some 14° absolute. Moreover, the value 24.18 for hydrogen has been got directly from experiment, whilst the other values have been obtained from semi-theoretical equations whose validity is subject to some doubt.

(To be continued).

OBSERVATIONS ON SOME CONTINUOUS INTRAMOLECULAR, AND AT FIRST REVERSIBLE, CHANGES EXTENDING OVER PROLONGED PERIODS OF TIME.

By R. J. FRISWELL.

(Concluded from p. 197).

PART II. Experimental.

On October 3rd, 1885, they were introduced into a small flask 0.25 grm. aminoazobenzene base in crystals, 5.0 grms. aniline hydrochloride crystals, and 15 c.c. water.

An almost colourless solution of the aniline salt was formed, in which the bright yellow crystals of aminoazobenzene base lay in a heap at the bottom. The flask was now rapidly raised to the boil for about one minute, and closely corked up.

The effect of the boiling was to cause the aminoazobenzene base to dissolve, forming the characteristic deep red solution exhibited by its hydrochloride. As the solution cooled, it became very much paler, and much aminoazobenzene base crystallised out as a bulky mass, while on the bottom of the flask were perhaps a dozen minute steel-blue needles of the hydrochloride.

The flask was put aside in a cool, badly lighted place, and when examined two days later, on the 5th, the steel-blue hydrochloride crystals had greatly increased in number. Daily examinations were made, and it was found that this change continued.

On the 12th, the base crystals were scarcely visible, and

on the 19th they had entirely disappeared, save some that had stuck to the sides of the flask above the liquid, and the whole lower part was full of the hydrochloride.

On the same day (October 3rd), another similar flask, No. 2, was started with the same quantities of the materials, but it was at once put aside in the cold without heating.

The same change occurred, though more slowly, but by the 19th the whole of the base crystals had vanished, and were replaced by exceedingly minute crystals of the hydrochloride.

On October 5th, another flask, No. 3, was started, an exact repetition of No. 2. It behaved in exactly the same way.

Some weeks later, when all traces of the base had gone, this flask, No. 3, was raised to the boil. On cooling, much base was seen to be regenerated, and nine days later the crystals of base were still visible, though the conversion into hydrochloride was slowly taking place.

No. 4 flask, started on October 5th, contained 0.25 grm. aminoazobenzene base, 5 grms. aniline nitrate, and 15 c.c. water. On boiling it, no change occurred; both base and aniline nitrate crystallised out unchanged. They remained unchanged for many years.

No. 5 flask, started the same day, contained 0.25 grm. aminoazobenzene base, 5 grms. aniline hydrochloride, 0.25 grm. free aniline, and 15 c.c. water. It was boiled; the base crystallised out somewhat darker in colour.

No. 6 flask, on the same day, consisted of 0.25 grm. aminoazo-base, 5 grms. chloride of ammonium, and 15 c.c. water. On cooling, the base crystallised out in splendid needles, and it remained unchanged for nearly twelve years, when the flask was destroyed.

On October 10th, No. 7 flask was started with the aminoazo-base and free aniline in molecular proportions as well as aniline hydrochloride as follows:—Aminoazobenzene base, 0.5 grm; aniline, 0.24 grm.; aniline hydrochloride, 10 grms.; water, 30 c.c. It was boiled, and, on cooling, the base crystallised out rather darker than before. No change took place. No crystals of the hydrochloride were visible.

Accordingly, on December 3rd, after an interval of forty-two days, the contents of the flask were vigorously shaken, and then, as nearly as possible, one-half was poured into flask 8. To it was added a single clean crystal of the aminoazobenzene hydrochloride. Thirteen days later no change had taken place in either. They were therefore each raised to the boil for one minute, and again put aside.

On April 27th, 1886, 131 days later, they were still unchanged, not a crystal of aminoazobenzene hydrochloride could be seen.

They were put aside in a dark, cool place till March 2nd, 1887, when, on bringing them to the light, each was found with the lower part filled with large steel-blue lustrous crystals of aminoazobenzene hydrochloride.

On February 1st, 1886, flask No. 1, which had in nineteen days completely changed its base into chloride, had remained from its starting 120 days; it was raised to the boil, and on cooling it had returned to its original appearance after charging, boiling, and cooling, *i.e.*, a little steel-blue hydrochloride lay on the bottom, above this a bulky mass of fine yellow crystals of the base.

These latter continued to diminish steadily, and seven days later, on the 8th, the base had entirely vanished, and the hydrochloride correspondingly increased. Thus the flask had twice gone through this series of changes.

The work which it has taken the amino-base fourteen days to do at the average temperature is undone by one minute's boiling. After that it takes six days at ordinary temperatures to re-enact the change.

The phenomena are most remarkable, when it is remembered that the effect of the boiling is to hasten the first stages of the change, for in flask No. 1 crystals appeared as soon as it was cool, while in flask 3, which was not boiled, several days elapsed before any showed themselves.

TABULAR VIEW OF EXPERIMENTS.

Substances engaged in reaction.	Date of commencement Into amidoazobenzene hydrochloride.	Date of completion	Number of days.	Character of vessel.	Remarks.
1. $C_{12}H_{11}N_3$, 0.25 grm. $C_6H_5NH_2HCl$, 5.0 grms. H_2O , 15 c.c.	Oct. 3, 1885.	Oct. 19, 1885.	16	Corked flask.	Boiled for a few seconds.
2. Same as No. 1.	Oct. 3, 1885.	Oct. 19, 1885.	16	Corked flask.	Entirely in the cold.
3. Same as Nos. 1 and 2.	Oct. 3, 1885.	Oct. 19, 1885.	16	Corked flask.	As No. 1 (<i>i.e.</i> , boiled).
4. $C_{12}H_{11}N_3$, 0.25 grm. $C_6H_5NH_2HNO_3$, 5.0 grms. H_2O , 15 c.c.	Oct. 3, 1885.	Unknown.	Over 550.	Corked flask.	In about 3000 days colour had formed.
5. $C_{12}H_{11}N_3$, 0.25 grm. $C_6H_5NH_2HCl$, 5.0 grms. $C_6H_5NH_2$, 0.28 grm. H_2O , 15 c.c.	Oct. 3, 1885.	Unknown.	Unknown.	Corked flask.	Experiment lost.
6. $C_{12}H_{11}N_3$, 0.25 grm. NH_4Cl , 5.0 grms. H_2O , 15 c.c.	Oct. 5, 1885.	No change.	No change after 4280 days.	Corked flask.	Boiling had no effect.
7—8. $C_{12}H_{11}N_3$, 0.5 grm. $C_6H_5NH_2HCl$, 10.0 grms. H_2O , 30 c.c. $C_6H_5NH_2$, 0.24 grm.	Oct. 10, 1885.	March 2, 1887.	All crystals in 405 days.	Corked flask.	Divided into two.
X. $C_{12}H_{11}N_3$, 0.5 grm. $2(C_6H_5NH_2)H_2SO_4$, 2.0 grms. H_2O , 15 c.c.	Mar. 3, 1887.	No change.	No change after 3900 days. None after 17 years.	Corked flask.	Boiling no effect.
Y. $C_{12}H_{11}N_3$, 1.0 grm. $C_6H_5NH_2HCl$, 20 grms. H_2O , 60 c.c.	Mar. 2, 1887.	Unknown.	Very slow.	Corked flask.	Cold. Still—after 3600 days—many fine crystals of base.
Tube 1. $C_{12}H_{11}N_3$, 0.5 grm. $C_6H_5NH_2HCl$, 5 grms. H_2O , 15 c.c.	Mar. 12, 1887.	Jan. 30, 1888. <i>t</i> 15—17°.	325 days all chloride.	Sealed tube.	Boiled.
Tube 2. $C_{12}H_{11}N_3$, 0.5 grm. $C_6H_5NH_2HCl$, 10 grms. $C_6H_5NH_2$, 24 drops. H_2O , 15 c.c.	Mar. 15, 1887.	Kept in well till Jan. 30, 1888. <i>t</i> 10—11°.	320 days, no change.	Sealed tube.	Boiled.
Tube 3. $C_{12}H_{11}N_3$, 0.5 grm. $C_6H_5NH_2HCl$, 10 grms. H_2O , 15 c.c. $C_6H_5NH_2$, 24 drops.	Mar. 14, 1887.	Unknown. Changed into colour. Boiled and sealed.	Colour formed.	Sealed tube.	Kept at about 49° C.
Tube 4. $C_{12}H_{11}N_3$, 0.25 grm. $C_6H_5NH_2HCl$, 5 grms. H_2O , 15 c.c.	May 16, 1894.	August, 1895. Not boiled. All hydro- but sealed chloride—440 days.	Colour is not decided in Oct., 1897—say, in 1219 days,—but June 4, 1900, gone almost as far as No. 4; Nov., 1900, quite gone—2370 days.		Colour suspected in middle of September, 1897.
$C_{12}H_{11}N_3$, 0.25 grm. $C_6H_5NH_2HCl$, 5 grms. H_2O , 20 c.c.	May 16, 1894. Boiled, and sealed hot.	Jan. 1, 1896. Nearly all hydrochloride.	Colour suspected in June, 1897 (<i>i.e.</i> , in, say, 770 days); undoubted in Sept., 1897; and complete March, 1898—say, 1219 days.		

THE ELEMENTS: VERIFIED AND UNVERIFIED.

By CHARLES BASKERVILLE, Ph.D., F.C.S., Smith Professor of General Chemistry, University of North Carolina.

(Concluded from p. 193).

LIST OF PROPOSED CHEMICAL ELEMENTS (*continued*).

Date.	Name.	Source.	Authority.	Reference.	Remarks.
1901	Euxenium earth I.	Euxenite from Bre- vig.	Hofmann and Prandtl.	Berichte, 34, 1064.	Differs from zirconium in certain reactions. Atomic weight 178 (calcd.) if it be tetravalent. Also another unknown substance present, giving chemical reactions quite different from I. Giesow and Honkheimer failed to secure either from purchased pure zirconium sulphate (<i>Zeit. Anorg. Chem.</i> , 1902, 32, 372).
1901	Euxenium earth II.	Euxenite from Bre- vig.	Hofmann and Prandtl.	Berichte, 34, 1064.	
1902	<i>Amarillium</i> .	Copper ore (British Columbia).	Courts.	Trans. Am. Inst. Min. Eng., advance sheet, New Haven Meeting, October, 1903.	In parting gold button observed peculiar behaviour. Hille- brand says ("Review Am. Ch. Res.", 1901, 9, 151):—"Eastern assayers had reported the metal in the ore to be platinum and palladium" (?).
1903	<i>Brillium</i> .	Coal ashes.	Reporter's fertile brain.	Washington Post, Nov. 18.	Special correspondence from Newark, N. J. Reported presence of material in coal ashes which produces more heat when placed under furnace than fuel bought from trust.
1903	"Radium-foil."	Zinc-bearing minerals.	Kunz and Baskerville.	Am. Journ. Sci., 1904 (see next).	Zinc oxide and sulphide, willemite, and kunzite (which contains zinc) fluoresce and phosphoresce with Roentgen rays, ultra-violet light, radium, and actinium prepara- tions, even shielded.
1903	New element (?).	Minerals from Mono Lake, California.	Kunz and Baskerville.	New York Acad. Sci., Octo- ber 6; Am. Journ. Science, January, 1904; Science, 18 (N.S.), 769.	Every mineral without exception and regard to chemical composition, from this lake phosphoresces with ultra- violet light. Considering the formation of these minerals, they appear to have some common constituent giving this response. Whether it be new cannot be stated, but the observations are sufficiently unique to place on record for subsequent investigation. See the full paper for other somewhat similar observations with other minerals.
1903	Tellurium X.	Tellurium.	Pellini.	Gazz. Chm. Ital., 33, 11, 35.	Maintains presence of constant small radio-active con- stituent with atomic weight about 212, which causes tellurium to hold its present anomalous position in the Periodic Table. (See Marckwald, Ber., 35, 2285).
1903	Berzelium.	Thorium.	Baskerville.	Presented before N. Carolina Section, American Chemi- cal Society, November 28; American Assoc. Adv. Sci., December 29.	Obtained by fractionating thorium chlorides during production by volatilisation. "Weisser dampf" of Berzelius, hence name. Oxide does not phosphoresce with ultra-violet light, while thorium oxide does. Atomic weight (im- pure material) 212.7, when regarded tetravalent.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1904.

By SIR WILLIAM CROOKES, F.R.S.

PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, April 16th, 1904.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 219 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 219 samples examined by us during the month, all were clear, bright, and well filtered.

There has been a deficit in the rainfall at Oxford during March; the actual amount of rain measured during the past month was 1.95 inches, and the average fall is 1.47 inches; thus we have a deficit of 0.42 inch, which, if subtracted from the previous excess of 2.20 inches, leaves an excess of 1.78 inches, or 33.3 per cent above the thirty-five years' average.

Our bacteriological examinations of 401 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 387 others from special wells, standpipes, &c., making 788 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	210
New River, filtered (mean of 80 samples) ..	11
Thames, unfiltered (mean of 27 samples) ..	7410
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 213 samples) ..	17
Ditto ditto highest	310
Ditto ditto lowest	0
River Lea, unfiltered (mean of 27 samples) ..	187
River Lea, from the East London Water Com- pany's clear-water wells (mean of 27 samples) ..	9

Of the 320 daily samples taken from the general filter wells of the Metropolitan Water Companies, nineteen samples, or 5.9 per cent, were sterile. Ten samples, or 3.1 per cent, contained more than 100 microbes, and of these, only three samples contained more than 150 microbes per c.c. The ten excess samples contained an average of 148 microbes per c.c. In February twenty-seven excess samples contained an average of 162 microbes per c.c.

Both the Thames and the Lea have now recovered from the effects of the abnormal floods which have been prevalent for so many months. The result is that both the chemical and bacteriological condition of the water supply has been manifestly improved, and may now be characterised as excellent for this period of the year.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

HAUSMANNITES FROM SWEDEN.

B. A. GÖRGET.

In a previous paper on "The Native Oxides of Manganese" (*Bull. Soc. Chim.*, 1893, p. 650), I found from 1 to 8 per cent of oxide of zinc in the Hausmannites from Ilmenau in Thuringia, and I observed that this oxide replaces an equivalent amount of manganous oxide in the saline oxide, $Mn_2O_3 \cdot MnO$.

Since that time I have been able to procure, by the help of M. G. Flint, a mineralogist at Stockholm, several beautiful samples of the same mineral coming, one from Jacobsberg, and the two others from Langbanshyttan.

With these specimens I determined to try and find out whether I could still detect the protoxide of zinc or another oxide, playing the same part in the constitution of the mineral as oxide of zinc does in that from Ilmenau.

In the samples analysed, the gangue, consisting of crystals of dolomite and Richterite, was easily eliminated. A single fine crystal, weighing 10 grms., furnished the sample for the analysis of Hausmannite from Langbanshyttan, No. 1; that of No. 2 from Jacobsberg was done on several very good isolated crystals; that of No. 3 from Langbanshyttan, consisted partially of crystals and partially of the massive portion which held them, without any gangue being apparent.

In the following table, opposite the figures given by the analysis, I have given the amount of oxygen contained in each of the acid or basic elements that the figures represent.

	No. 1. Langbanshyttan		No. 2. Jacobsberg		No. 3. Langbanshyttan	
	Analysis.	Oxygen.	Analysis.	Oxygen.	Analysis.	Oxygen.
H ₂ O ..	—	—	0.04	—	—	—
CO ₂ ..	0.37	0.27	0.50	0.36	0.19	0.14
Richterite ..	0.20	—	0.23	—	0.90	—
O ..	6.52	6.52	6.31	6.31	6.51	6.54
MnO ..	86.52	19.50	85.79	19.33	87.34	19.68
Fe ₂ O ₃ ..	4.30	1.29	5.75	1.92	3.47	1.04
ZnO ..	—	—	0.22	0.01	0.70	0.14
PbO ..	0.55	0.06	0.12	0.01	—	—
BaO ..	—	—	—	—	0.07	0.01
CaO ..	0.13	0.12	0.48	0.14	0.44	0.13
MgO ..	1.00	0.40	0.44	0.17	0.30	0.12
Alkalis ..	—	—	0.16	0.03	0.45	0.09
	99.89		100.07		100.40	

Considering only the peroxide of manganese that these three samples of Hausmannite contain, we notice that the ratios which exist between the weight of the oxygen of the protoxide of manganese, and that of the oxygen in those oxides above the protoxide, are as follows:—

$$\begin{aligned} &3 : 0.991 \text{ in No. 1} \\ &3 : 1.04 \text{ in No. 2} \\ &3 : 1.01 \text{ in No. 3} \end{aligned}$$

—ratios which are all very close to 3 : 1, which theory requires for pure Hausmannite.

But, associated with this peroxide, we find 5 to 7 per cent of different metallic oxides which ought not to be neglected, and of which it may be of use to determine the rôle. Should we look upon them as impurities deposited at the moment of crystallisation of the Hausmannite? This supposition would be very acceptable if the samples taken were from massive or pulverulent specimens; we cannot, however, admit it easily for samples 1 and 2, the mean results of which are obtained from a single crystal or form a small number of very good crystals. Another hypothesis is possible, and seems to be more natural; it consists of assuming that, in the Swedish Hausmannites, the sesquioxide of manganese and the sesquioxide of iron form the acid portion of the mineral, and that its basic portion comprises more particularly the protoxide of manganese, and to a small extent the other protoxides revealed by analysis.

To justify this second supposition we ought to find the

same ratio, 3:1, between the quantities of oxygen in the two peroxides and the total weight of oxygen in the protoxides, as in the pure Hausmannite.

The necessary calculations have been made for the three minerals analysed, using the figures given in the second columns of the analyses.

We determined, for each sample, the weight of the sesquioxide of manganese it contained, taking the figure for the oxygen above the protoxides; the oxygen contained in the actual amount of sesquioxide found added to that of the oxygen contained in the ferric oxide furnished the total amount of oxygen in the acid portion of each mineral.

The weight of the sesquioxide of manganese being known, it was easy, with the help of the figures found by the analysis, to estimate that of the protoxide of manganese combined with it; to the weight of the oxygen contained in this latter we added that contained in the other protoxides. The total of these figures should be diminished by the oxygen required to saturate the carbonic acid, so as to get exactly the amount of oxygen in the basic portion.

By proceeding in this manner we found the following ratios, in the three Hausmannites, between the atoms of oxygen in the acid elements and those in their basic elements:—In the Hausmannite from Langbanshyttan, No. 1, the ratio was 3:0.994; in that from Jacobberg, No. 2, the ratio was 3:0.99; and in that from Langbanshyttan, No. 3, the ratio was 3:1.02. These ratios are all as close to the theoretical figures, 3:1, as those found in the peroxides of manganese considered by themselves.

This manner of regarding them is confirmed by the synthetical experiments described in a paper which will appear shortly in the *Bulletin*.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 23.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, April 22nd, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A PAPER entitled "Calculation of Colours for Colour Sensitometers and the Illumination of 'Three Colour' Photographic Transparencies by Spectrum Colours" was read by Sir W. DE W. ABNEY.

In three-colour photography, photographs have to be taken through a red, a green, and a blue screen, the transparencies or prints from which are then viewed. The exact shades and hues of these screens depend on the light which is used for viewing the transparencies or on the colours employed in printing. The present paper confines itself to the former case. It is well to settle the colours which should be used by a reference to the spectrum, remembering that if any other colours, such as those transmitted through glasses, are employed, they must inevitably be less pure. The true guide to selection must be founded on the trichromatic theory of colour-vision, and the author has shown in a former paper that the position of the colours in the spectrum can be fixed with extreme accuracy. Any part of the spectrum below C towards A gives a colour which excites no other sensation than the red sensation. The green and the blue sensations are felt unmixed with any other colour-sensation, though rendered impure by the sensation of white, at b for the former, and near the blue lithium line in the spectrum of lithium for the latter. Any departure from these positions causes an excess of colour due to one of the three sensations, and is not therefore advisable to adopt it, as it increases the impurity of the mixed colours by adding still more and quite unnecessary white to the resulting hue. These three colours form the theoretical starting-point for the determination of the exact hue of the screens which have to be used. The determination of the exact hues of the screens is one which

presents some difficulties if resort is confined to the spectrum. A perfect photographic plate is one on which, if a spectrum be thrown, the opacities of deposit will represent luminosity exactly, or the transparency taken from such a negative will transmit white light at every portion of the image corresponding to the luminosity of the spectrum at that point. A perfect photographic plate does not exist, and hence we are driven to a plan which, not absolutely exact, is yet as near exactitude as possible. Any intermediate colour between the three standard colours can be matched in hue and luminosity by mixing the red and green together in proper proportions, or the green and blue. The colours of pigment can be matched by a mixture of two of the three chosen colours. The author has shown how, by means of luminosity equations, it is possible to arrange two pigments so that the components of any standard colour, say the green, are equal. Photographing the two pigments in which the green components are made equal, we must find some medium which will allow only such rays to pass as will make the two images of equal opacity. This will be a green of some kind. With more colours similarly treated we get an approach to colours at different parts of the spectrum, and we can then determine the screen to be used for any kind of plate which it is possible to use. The amounts of red, green, and blue existing in the red, yellow, green, and blue pigments and white were determined, and the luminosities being known the amounts of each of three spectrum-colours in luminosities were determined to make up the total luminosity of the pigment (or white). Supposing that a screen was sought for which would give the proportions of red on the photographic plate. The luminosities had to be so reduced in the pigments chosen that the red component in each was of the same luminosity. This was effected by making rings of the colours on a disc and cutting off part of the rings by black. We thus have a disc in which all the rings have equal red luminosity. Having got three separate discs in which the red, the green, and the blue components are made equal respectively, the screens for the camera were found by altering the hue till the opacities in the negative of all the rings were equal. Having obtained the negatives, transparencies are made from them. These are usually placed in a triple lantern with the three colours behind the objective. The light coming through each is so arranged that the white formed by their mixture is of the same quality as sunlight; but as they are impure colours they give more white in the picture than is to be found in nature. Sir William Abney showed how to illuminate the transparencies by using spectrum-colours, placing slits on the three colours which answer best to the three colour-sensations.

A paper on "Normal Piling as connected with Osborne Reynolds's Theory of the Universe," was read by Prof. J. D. EVERETT.

The closest arrangement of equal spheres *in plano* is the triangular one in which each is touched by six. To obtain the closest packing in space, the pile of spheres must consist of a succession of these tiers.

In building such a pile, the laying of each successive tier gives a choice between two different positions of this tier relative to its predecessor. Suppose two regular tetrahedrons to be placed base to base, so that one is the reflection of the other relative to the base; and let the edges of one of these tetrahedrons be parallel to the six lines which join the centres of four spheres in mutual contact (say in the first and second tiers). The peculiarity of "normal piling" is that this rule holds in passing from each tier to the next, through the whole pile. The other alternative is represented by the edges of the second tetrahedron, and gives equally close packing. If we use the two tetrahedrons alternately as our guides in laying successive tiers, we obtain the system of closest piling which comes next in simplicity to normal piling. It may be called "anti-normal piling."

In normal piling every sphere belongs to six lines of spheres which are continued through the whole pile. They

are parallel to the six edges of the standard tetrahedron. In anti-normal piling there are only three such lines instead of six.

In normal piling every sphere belongs to four sets of triangularly arranged tiers, which are parallel to the four faces of the tetrahedron. In anti-normal piling there is only one set, instead of four.

Again, in normal piling there are three sets of squarely arranged tiers, their planes being at right angles. In anti-normal piling there are only fragmentary traces of square arrangement.

Prof. O. Reynolds's theory asserts that the universe is composed of infinitely hard equal spherical grains in approximately normal piling, which, on striking, rebound without loss of relative velocity; their free paths being infinitesimal compared with their diameters, except in places where the grains are out of gear (called surfaces of misfit). A spherical surface of misfit is the simplest kind of atom of ordinary matter, and is propagated as a solitary wave through the surrounding grains, by the transfer of grains across it in the reverse direction.

The excitation of electricity by friction is explained as the tearing away of a cluster of grains from one part of a normal pile and thrusting it into another part. Disarrangements of opposite kinds are produced at the two places, each involving diminished closeness of packing. Magnetism is explained as a rotational displacement of a spherical cluster of grains, sufficient to cause grains near the equator of the sphere to slip a tooth (as it were) in their gearing with the grains outside, while grains nearer the poles have not moved far enough to slip a tooth. The spherical cluster is thus subjected to rotational strain and stress.

Attractions and repulsions are manifestations of a tendency of disarranged grains towards closer packing; a tendency due to the continual impacts from without, which (as in the kinetic theory of gases) are equivalent to external hydrostatic pressure.

The paper maintains that, in a struggle for existence between different kinds of closest piling, represented by separate clusters with room to change their arrangements, normal piling possesses great advantages, first, in its six sets of lines of spheres, which serve as battering rams, and secondly, in its four sets of tiers in closest array, which facilitate the coalescence of adjacent clusters.

A "Note on the Diffraction Theory of the Microscope as applied to the case when the object is in motion," by Dr. R. T. GLAZEBROOK, was taken as read.

According to the Abbe theory of microscopic vision, when a grating is placed on the stage of a microscope and illuminated by plane waves, diffraction images are formed in the focal plane of the object-glass and the images in the view-plane result from these, and this is undoubtedly true. The following difficulty has, however, been raised: if the grating be moved in its own plane in a direction perpendicular to the ruling, the diffraction images do not change, those seen in the view-plane move; how then can the latter images be due to the former? The answer lies in the fact that in the above argument the effect of the differences of phase among the diffracted images has been neglected. The diffracted images are not all in the same phase, their relative phases are altered by shifting the grating, and the image pattern in the view-field is altered in consequence. A simple case is considered in the paper, and it is proved that the image in the view-plane may change without an alteration in the position of the diffracted images.

An Automatic Gas-pump was exhibited by Mr. C. E. S. PHILLIPS.

The apparatus is constructed upon a plan which enables the pump, when once set in operation, to continue automatically and to produce as perfect a Torricellian vacuum as is possible. It has been devised with a view to providing a comparatively portable machine suitable for special laboratory work, or for researches requiring pro-

longed pumping, and consists of three distinct parts, viz.: a small motor-driven mechanical pump, a four-way control valve, and a modified Toeppler apparatus by which the final vacuum is obtained. Experiment has shown that the apparatus is fairly rapid in its action. In a preliminary trial a Röntgen-ray bulb of 200 c.c. capacity was exhausted in half an hour. The glass work is easily removed for cleaning or repairs, and the wood supports are fitted with adjustable brackets. The height of the complete apparatus is 18 inches.

There was also an exhibition of spectroscopic and other scientific apparatus by Mr. PETER HUELL.

NOTICES OF BOOKS

Baltimore Lectures. By LORD KELVIN. London: C. J. Clay and Sons. Pp. 694.

THIS volume is based upon the course of twenty lectures delivered by Lord Kelvin (Sir W. Thomson) in 1884 at the Johns Hopkins University, his subject being "Molecular Dynamics and the Wave Theory of Light." Nearly half the volume is occupied by twelve appendices on "Allied Subjects"; and as many of the lectures themselves have been largely re-written, it may be said to contain all that is known of the branches discussed.

We have read the book from cover to cover, hoping to find something easy as a basis for review, but when we remind our readers that the lectures were delivered to an audience of scientific men, many of them of world-wide reputation, and that the assumption of "common knowledge" was pitched at a correspondingly high level, we may be excused for saying we propose to make no comments as to their accuracy and value. The appendices are on a different footing; they have been written at different periods and for different audiences, and, excepting for the mathematics, they are both interesting and comparatively easy to understand, so much so that in two instances we disagree with Lord Kelvin's conclusions, and venture to set forth the grounds for so doing.

In Appendix B, Lord Kelvin describes some careful experiments he made with regard to the path of a particle in enclosed areas of different shapes, and having summed the kinetic energy along the co-ordinates during several hundred flights, he arrives at the conclusion that the Boltzmann-Maxwell doctrine as to the equality of the energy in all directions is not justified.

It seems to us that the experiment fails for two reasons:—Firstly, as only one particle is considered, the effect of collisions in "averaging" energy is ignored; and, secondly, "several hundred flights" are altogether inadequate to give a true idea of the average direction or motion of a single particle.

Maxwell considered a group of many millions of atoms, and stated that they would behave in a certain way. Lord Kelvin examines a single particle and finds that it does not, in an extremely limited period, harmonise with Maxwell's doctrine. Probably Maxwell would have been astonished if it did.

The Boltzmann-Maxwell doctrine may be wrong; in fact, Lord Kelvin gives other reasons, which appear conclusive, for stating that it is, but it is not obvious how the experiments described have any value.

Appendix D deals with a speculation as to the amount of matter in the universe in an interesting but unconvincing manner. Lord Kelvin says on page 534:—"Hence, if the thousand million suns had been given at rest twenty-five million years ago, uniformly distributed throughout the supposed sphere (of 3.09×10^{16} kilometres radius), many of them would now have velocities of 20 or 30 kilometres per second, while some would have less, and some probably greater velocities than 108 kilometres per second; or, if they had been given thousands of millions of years ago at

rest so distributed that now they were equally spaced throughout the supposed sphere, their mean velocity would now be about 50 kilometres per second. This is not unlike the measured velocities of stars, and hence it seems probable that there might be as much matter as one thousand million suns within the distance 3.09×10^{16} kilometres.

Surely, in either of the assumed cases, the paths of all the stars would be sensibly centripetal, which the observed paths of the few stars recognised to be in motion is not; this consideration alone appears to put the assumed "initial state" out of court. Again, the visible stars are not by any means even approximately uniformly distributed in space, and it is highly probable that they have not been so, so recently as twenty-five million years ago; whether they might have been during the longer but vaguer period of "thousands of millions of years ago" is another question, but if they were, it is reasonably certain, from their present distribution and the paths of such of them as are approximately known, that they were not then at rest. Again, considering the few stars whose parallaxes have been measured, and the uncertainty attaching to the values of the parallaxes and proper motion, it is taking full advantage of the figures to say "this is not unlike the measured velocities of stars."

So it seems that if one thousand million suns had been distributed a certain long time ago in a manner in which they were not, or if they had been an uncertain time ago so distributed, that they would now be distributed in a manner in which they are not, their mean velocities would be approximately equal to the assumed mean velocities of the visible stars, though their directions would be different. "Hence it seems probable that there might be as much matter as one thousand million suns within the distance 3.09×10^{16} kilometres." Well, there may be; but there is not much reliable evidence either way.

The Electrolysis of Water: Processes and Applications.

By VIKTOR ENGLEHARDT. Authorised English Translation by J. W. RICHARDS, M.A., &c. With 90 Figures and 15 Tables in the Text. Easton, Pa.: The Chemical Publishing Company. 1904. Pp. 140.

THIS volume is the first of a collection of monographs of applied electrochemistry, and is devoted to a description of the processes used for the electrolysis of water.

The different processes for effecting this decomposition are divided into three principal groups:—

- A. Processes and apparatus for the separate production of oxygen and hydrogen. Sub-divided into—(a) With porous diaphragms of non-conducting material; (b), with complete non-conducting partitions; and (c), with complete or perforated conducting partitions.
- B. Processes and apparatus for the electrolysis of water without separation of the gases (production of detonating gas).
- C. Processes for the simple evolution of oxygen—(a) Through depolarisation at the cathode; and (b) by the precipitation of metal at the cathode.

All the above processes are fully described in the third and most important section, at the end of which is a table giving them all in chronological order.

In the above section, and from the applications described in it, it may be assumed that the question of the industrial electrolysis of water for the purpose of obtaining oxygen and hydrogen has been solved in numerous ways, but the applicability of these processes has become much more of a practical question in these days of cheap power. In Section IV. the author describes various installations and their capacity of competing commercially with other methods, and he gives in compact form the cost of plant and cost of working of these different processes.

Special applications of the uses of oxygen and hydrogen, and the mixed gases, are described at the conclusion of the book, and some new propositions concerning their use are alluded to at length.

Besides forming a valuable collection of processes for

the production of oxygen and hydrogen by the electrolysis of water, this volume is rich in suggestions of ways and means for overcoming difficulties in electrochemical operations in general, and will be found of value to electro-chemists engaged in other branches of the subject.

The book closes with an index of author's names, which, though useful to those who are very well acquainted with the subject, by no means makes up for the lack of a general index; there is, however, a very full table of contents, and this must serve in its place.

Practical Chemistry. Part II. By WILLIAM FRENCH, M.A., F.I.C., and T. H. BOARDMAN, M.A. London: Methuen and Co. 1904. Pp. 126.

PART I. of this book was published as long ago as 1900, and was noticed in this column in May of that year.

PART II., which has recently appeared, continues as far as possible according to the scheme adopted in Part I.

Chapters I. and II. are on the properties of gases, such as the effects of changes of temperature and pressure, and their densities, solubilities, and diffusion. Then follow several chapters on the laws of chemical combination, equivalents, the atomic theory, symbols, &c. Chapter VIII. is on sulphur and its compounds, and deals with this subject in an adequate manner, while Chapters IX. on nitrogen and X. on carbon, deal in a similar manner with some of the compounds of these elements.

The illustrations are superior to those so often met with in this class of book, and we are glad to find the authors have risen superior to the well known picture of a wash-bottle, a funnel, or a piece of platinum wire. We must, however, call attention to the inconvenient arrangement of the table of contents; the page numbers of Chapters V. and VII. are not given at all, and we find that the pages given in the other cases do not refer to the page on which the chapters commence, but to certain paragraphs in these chapters. Still, this is only a small matter, and does not detract from the value of the book as an educational work.

Calculating Tables. By Dr. H. ZIMMERMANN. London: Asher and Co.

THIS work contains a multiplication table of all numbers to 1000 by 1 to 100, and various tables of squares, cubes, square and cube roots, functions of π , and other quantities which are continually being used in calculations; the object being, as stated in the preface, to avoid the use of logarithms as much as possible. The practical value may be gauged by the fact that the preface is dated Berlin, 1889, and after the experience of fifteen years it has been considered a judicious speculation to publish an English edition.

The compiler of the tables is so confident of their accuracy that he has offered a reward to any user of the tables who may detect any errors in them. As this challenge is now fifteen years old, we may conclude that their claim to accuracy is vindicated.

As an adjunct to the usual tables of logarithms these tables should prove useful to many persons.

Introduction to Physical Chemistry. By JAMES WALKER, D.Sc., &c. London: Macmillan and Co. Pp. 364.

THIS book, originally published in 1899, has now reached its third edition, which is fair evidence of its value.

It is clearly written throughout, and the mathematical expressions are kept to a minimum, such as should be within the capacity of every student to understand.

A valuable feature of the work is the system of references at the end of most chapters to the original papers on the latest development of the subject matter treated of. Many of these references are to papers published in 1903; so it may be seen that the author has done as much as is possible to keep his work abreast of the times.

The work is worthy of a place on the shelves of every chemist's library.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. CXXXVIII, No. 13, March 28, 1904.

Certain Physical Constants of Phosphorus Fluorides.—Henri Moissan. The determination of the melting- and boiling-points of the various fluorides of phosphorus presents certain difficulties, on account of their easy decomposition by water. In the preliminary experiments the author tried to determine these constants by means of a thermometer, but the necessity of operating on a very small quantity of material and in a perfectly closed vessel rendered the equilibrium of temperature between the liquid and the thermometer doubtful. His determinations were finally made by means of a thermo-electric cell, and the melting- and boiling-points of the three fluorides of phosphorus, under normal pressure, are shown by the following table:—

	Melting-point.	Boiling-point.
PF ₃	-160°	-95°
PF ₅	-83°	-75°
PF ₃ O	-68°	-40°

Separation of Chromium and Vanadium.—Paul Nicolardot.—Already inserted in full.

Preparation of Ether Oxides by means of Magnesium Compounds and Halogen Methylic Ethers, X.CH₂OR.—J. Hamonet.—M. Henry used the action of halogen methylic ethers, X.CH₂OR, on organo-zinc compounds to show that, by means of successive substitutions, methylic alcohol can be transformed into all its superior homologues: (CH₃)₂Zn + 2XCH₂OR = ZnX₂ + 2CH₃CH₂OR. The author finds that this reaction applies equally well to M. Grignard's magnesium compounds, R.MgX + XCH₂OR = MgX₂ + R.CH₂OR. By applying this method, the author prepares amyloxypropylic ether, C₅H₁₁OC₃H₇, boiling at 130°; benzyloxy-methylic ether, C₆H₅CH₂OCH₃, boiling at 170°; and phenylethoxy-methylic ether, C₆H₅CH₂CH₂OCH₃, a liquid never before obtained, boiling at 189°—190°.

Phospho-nitrated Bases of the Type (RNH)₃P=NR.—P. Lemoult.—In a previous investigation the author proved the existence of a new phosphorus base derived from aniline:—Trianilidophenylphosphimide, (C₆H₅NH)₃P=NC₆H₅. He now prepares certain homologous amines of aniline, particularly the *o*-toluidine and the *as-m*-xylylidine. The salts derived from these two series can be considered as derived from an analogous monacid base into an anilide base of the general type (RNH)₃P=NR(R, C₆H₄ or C₆H₃ or C₆H₂), becoming a salt in the manner of ammonia by simply fixing the elements of a molecule of monobasic acid. It appears that the basic activity and the stability of the base itself diminish as it rises in the series.

Application of Acetylene Gas to the Heating of Germination Stoves by means of an Automatic Regulator of Temperature.—H. Joffrin.—The author describes a germination stove which can be used with acetylene gas when ordinary coal-gas is not attainable. A drawing is given of the apparatus.

MISCELLANEOUS

Protection of Steel from Corrosion.—Experiments have been made recently by Prof. C. L. Norton, of the Insurance Engineering Experiment Station, Boston, U.S.A., on the best methods of protecting steel used in buildings from corrosion. In some of the high buildings in America the question of the corrosion of the steel

footings is one of the utmost importance; when embedded in damp ground. Under such conditions the steel may be corroded by electrolysis from leaking currents from an electric rail or tramway, though dry steel will carry electric currents without injury. It has been found that Portland cement concrete affords perfect protection to steel embedded in it. The specimens of steel were cut to about 3 inches by 1 inch, and were of all thicknesses from 1/50 inch to 1 1/4 inch. Some were cut dry, some in oil, some in water, so that all conditions met with in regular practice should be included. Each piece was weighed and calipered at several points, and incorporated in a block or brick of concrete sufficiently large to cover it everywhere to a depth of one inch and a-half. The blocks were divided into three groups, one group being set out of doors, one stored in a damp and odoriferous cellar, and the third being treated in the "corroders," or steam and carbon dioxide tanks. Other specimens were further exposed in tide water, in sewers, and over furnaces with constant contact with furnace gases. After varying lapses of time, from one to nine months, the specimens were broken out of the briquettes, cleaned, weighed, and calipered. Not one specimen showed any sensible change in weight or dimensions except where the cement had been poorly applied.

The Precipitation of Colloidal Solutions of Sulphide of Arsenic.—F. W. Kuster and G. Dahmer.—In a preceding communication the authors have shown that sulphuretted hydrogen reacts quantitatively on aqueous solutions of arsenic acid, transforming them into sulphide, the sulphide formed remaining for a longer or shorter time in solution in the colloidal state (*Zeit. Anorg. Chem.*, vol. xxxiii., p. 705). This colloidal solution is precipitated very rapidly by coarsely ground Iceland spar. The other substances tried, such as heavy spar, precipitated sulphate of baryta, wood-charcoal, oxide of copper, and powdered glass, are much less active. The precipitation is further considerably facilitated by agitation and by the use of a large excess of the precipitating agent. The use of heavy spar (or of the other substances tried) does not seem, as mentioned by Vanino (*Ber.*, vol. xxxv., p. 662), to show a distinction between true solutions and colloidal solutions; for as we should preferably operate in the presence of a considerable quantity of the precipitating agent (100 parts of this latter to 1 part of the colloid to be precipitated, for example), it is to be feared that the materials really in solution are only more or less precipitated by reason of surface absorption.—*Zeit. Anorg. Chem.*, vol. xxxiv., p. 470.

MEETINGS FOR THE WEEK.

- MONDAY, May 2nd.—Royal Institution, 5. Annual Meeting.
— Society of Arts, 4.30. (Cantor Lectures). "The Majolica and Glazed Earthenware of Tuscany," by Prof. R. Langton Douglas, M.A.
— Society of Chemical Industry, 8. "Determination of Minute Quantities of Bismuth in Lopper Ores" and "Determination of Minute Quantities of Arsenic in Copper Ores and Metallurgical Products" by T. C. Cloud.
"Testing Colloids," by Prof. E. J. Mills and A. Gray.
TUESDAY, 3rd.—Royal Institution, 5. "Meteorites," by L. Fletcher, F.R.S., &c.
— Society of Arts, 4.30. "Canada and Great Britain," by W. L. Griffith.
WEDNESDAY, 4th.—Society of Arts, 8. "Statistics of the World's Iron and Steel Industries," by William Pollard Digby.
— Society of Public Analysts, 8. "Cod-liver and other Fish Oils" and "Note on Mushroom Ketchup," by J. F. Liversidge. "Note on some Constants obtained in the Examination of Margarine," by Edward Russell and V. H. Kirkham. "Note on the Estimation of Sugars in Concentrated Malt Extract," by A. R. Ling and Theodore Readle.
THURSDAY, 5th.—Royal Institution, 5. "Great Britain and Europe (1763—1793)," by Arthur Hassall M.A.
— Chemical, 8. "Slow Combustion of Ethane," by W. A. Bone and W. E. Stockings. "Note on

the Hydrolysis of Starch by Diastase," by J. S. Foid. "The Resin Acids of the *Coniferae*—Part I. The Constitution of Abietic Acid," by T. H. Easterfield and G. Bagley. "The Action of Radium Rays on the Halides of the Alkali Metals, and Analogous Effects produced by Heat," by W. Ackroyd. "The Dynamic Isomerism of Glucose and of Galactose—Solubility as a means of Determining the Proportions of Dynamic Isomerism in Equilibrium," by T. M. Lowry. "A Study of the Substitution Products of *α*-Tetrahydro-*α*-naphthylamine, *α*-4-bromotetrahydro-*α*-naphthylamine, and *α*-Tetrahydro-*α*-naphthylamine-*α*-sulphonic Acid," by G. T. Morgan, Miss F. M. G. Mickelthwait, and H. B. Winfield. "The Additive Products of Benzylbenzoiniline with Methylacetoacetic Ester and Acetoacetic Ester," by F. E. Francis and Miss M. Taylor.

FRIDAY, 6th.—Royal Institution, 9. "Anthropoid Apes," by P. Chalmers Mitchell, D.Sc.
Physical, 8. "An Experiment with Lubricating Oil," by W. A. Price. "Some Instruments for the Measurement of Large and Small Alternating Currents," by W. Duddell. Exhibition of Apparatus from the National Physical Laboratories.

SATURDAY, 7th.—Royal Institution, 3. "Sonata Style and the Sonata Forms" (with Musical Illustrations), by Donald Francis Tovey, B.A.

BACTERIOLOGY.

KING'S COLLEGE, LONDON.

Professor HEWLETT, M.D., D.P.H.
H. S. WILSON, M.B., D.P.H.

COURSES OF INSTRUCTION are given in GENERAL BACTERIOLOGY, the BACTERIOLOGY of FERMENTATION, and for the Examinations of the Institute of Chemistry. The Laboratories re-open on May and Students may enter at any time. Vacation Course, AUGUST 3rd to 10th.
For Syllabus and further information, apply to the SECRETARY or to Professor HEWLETT.

LONDON HOSPITAL MEDICAL COLLEGE. (UNIVERSITY OF LONDON).

The Summer Session commences on May 2.

The Hospital is the largest in England, nearly 800 beds. In-Patients last year, 13,120; Out-Patients, 182,903; Accident, 31,879; Major Operations, 3989.
Appointments.—80 Qualified Appointments are made annually, and more than 180 Dressers, Clinical Clerks, &c., are appointed every three months.

Scholarships and Prizes, Enlargement of the Hospital and College, Athletic Ground, Residence, &c.
For Particulars of the above, and for Prospectus giving full information as to Course of Study, Fees, &c., apply to—

MUNRO SCOTT, Warden.

Mile End, E.

E. GEORGE & SONS, BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.

Are OPEN to PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1838 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

Director required to invest £5000 to £7000 in a large Chemical Manure Manufacturing Business on an extensive scale. Security certain. Reason of requirement, death of former Director.—Write to K. B., care of Gould's Advertising Agency, 54, New Oxford Street, London, W.C.

MACMILLAN'S BOOKS ON CHEMISTRY. Fractional Distillation.

By SYDNEY YOUNG, D.Sc., F.R.S., Professor of Chemistry in University College, Bristol. With 73 Illustrations.

Crown 8vo, 7s. 6d.

CHEMICAL TRADE JOURNAL.—Supplies a long-felt want. . . . The whole of the chapters are easy and pleasant reading, and tempt the reader onward to the conclusion. . . . We feel sure that every chemist who is interested in, or engaged with, any manufacturing process in which distillation is practised, will feel genuine pleasure in perusing this work, in studying the points of the various chapters, and in repeating some of the many experiments so fully described by the author."

SECOND EDITION, REVISED AND ENLARGED.

A SYSTEMATIC SURVEY OF THE ORGANIC COLOURING MATTERS.

Founded on the German of Drs. G. SCHULTZ and P. JULIUS. Revised throughout and greatly Enlarged by ARTHUR G. GREEN, F.I.C., F.C.S., Professor of Tindforical Chemistry at the Yorkshire College, Leeds; late Examiner in Coal-tar Products to the City and Guilds of London Institute

Imperial 8vo, 21s. net.

Professor R. MELDOLA in "NATURE".—"It is as indispensable as its predecessor to all who are in any way concerned in this branch of chemistry and of chemical technology."

THE CHEMISTRY OF PLANT AND ANIMAL LIFE.

By HARRY SNYDER, B.S.,

Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Agricultural Experiment Station.

Globe 8vo, 6s. net.

GUARDIAN—"Valuable manual . . . clearly and attractively written."

ELEMENTS OF INORGANIC CHEMISTRY.

By HARRY C. JONES,

Associate Professor of Physical Chemistry in the

Johns Hopkins University.

Crown 8vo, 6s. 6d.

ROYAL COLLEGE OF SCIENCE MAGAZINE.—"We can without hesitation recommend this book to elementary students."

THEORETICAL ORGANIC CHEMISTRY.

By JULIUS B. COHEN, Ph.D., Lecturer on Organic Chemistry, The Yorkshire College, Lecturer in the Victoria University.

Globe 8vo, 6s.

NATURE—"The book is well printed, and the proofs have evidently been very carefully corrected. Taken as a whole, we consider Dr. Cohen's book a very useful compilation."

A COLLEGE TEXT-BOOK OF CHEMISTRY.

By IRA REMSEN, President of Johns Hopkins University.

Extra Crown 8vo, 8s. 6d. net.

GUARDIAN—"The author's skill in writing elementary textbooks is well known, and this work displays the features by which his other writings of the kind are characterised."

THIRD EDITION NOW READY.

INTRODUCTION TO PHYSICAL CHEMISTRY.

By JAMES WALKER, D.Sc., Ph.D., F.R.S.,

Professor of Chemistry in University College, Dundee.

Third Edition. 8vo, 10s. net.

CHEMICAL TRADE JOURNAL.—"A work we can earnestly advise the advanced chemist to study."

THE PRINCIPLES OF INORGANIC CHEMISTRY.

By WILHELM OSTWALD.

Translated with the Author's sanction by ALEXANDER FINDLAY, M.A., B.Sc., Ph.D. With 122 Figures in the Text.

8vo, 18s. net.

NATURE—"Prof. Ostwald's style is excellent, and full justice is done to it by Dr. Findlay's translation; hence the book is most readable and interesting. . . . It is unnecessary to mention that the work is entirely up to date."

MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2319.

PHYSICAL CONSTANTS AT LOW TEMPERATURES.*

I. THE DENSITIES OF SOLID OXYGEN, NITROGEN, HYDROGEN, &c.

By Prof. JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

(Concluded from p. 207).

5. With these values for the molecular volumes at absolute zero of oxygen, nitrogen, and hydrogen, namely, 21.21, 25.49, and 24.18 respectively, and knowing that the molecular volume of ice at absolute zero is 19.21 and of carbonic acid is 25.7 as deduced from a study of the coefficients of expansion at low temperatures, we can find the contraction or expansion on the assumed hypothetical production of these compounds from their elements at the zero of temperature ("Coefficients of the Cubical Expansion of Ice, Hydrated Salts, Soluble Carbonic Acid, and other Substances at Low Temperatures," *Roy. Soc. Proc.*, vol. lxxiii.).

Thus 100 volumes of mixed solid hydrogen and oxygen become, after combination, 55.22 volumes of ice, or there is a contraction of 45 per cent. This is of the same order of magnitude as for N_2O and Li_2O , whose contraction from solid oxygen, solid nitrogen, and metal amounts to 60 per cent. On the other hand, the production of carbonic acid from diamond ($V_0 = 6.82$) or graphite ($V_0 = 10.44$) and solid oxygen gives in the former case a slight expansion of 41 per cent, but in the latter case a slight contraction of 3 per cent.

The case of carbonic oxide ($V_0 = 24.5$) is interesting; produced from diamond and oxygen it expands by 74½ per cent, and from graphite and oxygen it expands by 54½ per cent, but on the addition of another atom of oxygen the resulting product, carbonic acid, undergoes a contraction of 27 per cent.

6. Berthelot made a minute examination of the values of $d(pv)/dp$ in reduced co-ordinates for eight substances whose critical temperatures range from that of carbonic acid to that of hydrogen; and came to the conclusion that the co-volume is one quarter of the critical volume, at least for low pressures ("Sur les Theromètres à Gaz. Trav., et Mém. Poids et Mesures," vol. xiii.).

Guldberg (*loc. cit.*) from a careful graphical discussion of Young's results, arrived at the conclusion that the critical volume is 3.55 times the volume at absolute zero.

An independent examination of the reduced curve for Young's fluorobenzene, showed that the reduced volume for a reduced pressure between 0.05 and 0.10 is very approximately 0.4; in other words, that the critical volume is two and a-half times the co-volume. And it is to be noted that the variations of the reduced volume in this neighbourhood are very slight compared with the change of the reduced pressure. Further, this range of reduced pressure will cover the extent of the present experiments whatever may eventually prove to be the value of the real critical pressure. My old experiments gave as a maximum a critical pressure of a little over 15 atmospheres.

Hence taking Van der Waals's $b = 12$ for hydrogen, these results give respectively 48 c.c., 42.6 c.c., and 30 c.c. as the critical volume, with the corresponding critical densities, 0.0208, 0.0235, and 0.033.

What further considerations can be brought to determine between these results? Van der Waals gives, for corre-

sponding states of two bodies, the equation ("Continuity, &c.," English translation, p. 491)—

$$\frac{d}{d'v} = \frac{M}{M'} \frac{t}{t'} \frac{p}{p'}$$

where d is density and M is molecular weight. Now in the liquid states for moderate pressure, the density changes but slightly, hence we may assume with very little error that the boiling-point densities belong to corresponding states. Comparing, therefore, hydrogen with oxygen, we get—

$$\frac{0.070}{1.138} = \frac{2}{32} \frac{t}{t'} \frac{155}{50} \text{ or } \frac{t}{t'} = 3.15$$

and comparing hydrogen with nitrogen we have—

$$\frac{0.07}{0.79} = \frac{2}{28} \frac{t}{t'} \frac{127}{35} \text{ or } \frac{t}{t'} = 2.93$$

hence, taking the mean, we have for hydrogen $t/t'p = 3.04$. Now, Van der Waals's theory makes $p_c v_c/t_c = \frac{8}{3} R$, but experiment seems to require $p_c v_c/t_c$ to be equal to $\frac{1}{3} R$, and when p is measured in atmospheres, $R = 41.0183$ for hydrogen, for which, therefore,—

$$\frac{p}{t} = \frac{41.0183}{3.77} = 10.8801$$

This gives $v_c = \frac{10.8801}{3.0} = 35.93$, and the critical density

as 0.0285, a result midway between that got from Guldberg's ratio and that derived from Young's reduced fluor-benzene.

Further experimental results can be brought to bear on the question. I have recently measured directly the heat of vaporisation of liquid hydrogen at the boiling-point, and find it to be not more than 125 calories per gram. Assuming the Rankine equation $\log_{10} p = A - B/t$, the molecular heat of vaporisation is $2B \log_{10} 10$. Hence we get $B = 54.34783$; and determining A from the values of p and t at the boiling-point we have in atmospheres,—

$$\log_{10} p = 54.34783 \left(\frac{1}{20.5} - \frac{1}{t} \right)$$

Now, at the critical point we have found $t_c = 3.04 p_c$, hence combining these results we have finally,—

$$t_c = 33.88^\circ, \text{ and hence } p_c = 11.145 \text{ atmospheres.}$$

Before leaving these results we may write the Rankine equation in Van der Waals's form, namely—

$$-\log t = \frac{54.34783}{t_c} \frac{1-m}{m}$$

where t and m are the reduced pressure and temperature, and Van der Waals's f is $54.34783 t_c$, or with the above result 1.604, about half the usual value of f . In like manner Trouton's constant, namely, the ratio of the molecular latent heat to the absolute temperature of the boiling-point, is 125.205 or 6.096, again only about half the usual value.

In this connection we may refer to Olszewski's experimental observation of the temperature, 192 absolute, at which the Joule-Thomson effect vanishes when the expansion is from a great pressure, in this instance between 110 and 117 atmospheres. With the usual Van der Waals's notation we may express the connection between this inversion temperature and the critical temperature in either of the forms,—

$$t = \frac{27}{4} \left(\frac{v-b}{v} \right)^2 \cdot t_c \dots \dots \dots (9),$$

or

$$t = 3 \left(1 + \frac{1}{2} \sqrt{1 + \frac{p}{9p_c}} \right)^2 \cdot t_c \dots \dots \dots (10),$$

the former equation shows that for small pressures and consequent values of v so great that b may be neglected

* A Paper read before the Royal Society, March 17, 1904.

in comparison with v , the critical temperature is $4/27$ of the temperature of inversion. But when the pressure is great, the ratio b/v cannot be neglected, and the critical temperature is a greater multiple of the temperature of inversion. The second of these equations shows that the initial pressure must not exceed nine times the critical pressure. Assuming a critical pressure of 16 atmospheres for hydrogen, and taking $p = 117$ atmospheres and $t = 192^\circ$, this equation gives the critical temperature as 42° absolute. Again, for $p_c = 15$ atmospheres, $t_c = 46^\circ$ and for $t_c = 32^\circ$, $p_c = 41$ atmospheres.

Results derived from a discussion of similar equations depending on Clausius's formula, Berthelot's "modified" Van der Waals's, or Reinganum's formula, are still farther from the value we expect.

In part explanation of this failure it is to be noted that these formulæ are but the best theoretical approximations we have at hand, and while they are useful within short ranges we can hardly expect the same accuracy over a temperature range of five or six times the critical temperature.

Again, for a very large number of bodies the product of a , the co-efficient of expansion at the boiling-point, and the critical temperature is constant and about 0.6 to 0.7.

Thus for oxygen, from equation (2), we have $at_c = 0.61$.

For nitrogen we get $at_c = \frac{0.0750}{0.8042 \times 15} \times 127 = 0.79$, but

for hydrogen we have $\frac{0.0054}{0.07 \times 5.8} \times 34 = 0.45$, and even if we take the critical temperature as high as 42° , at_c only reaches 0.56.

7. There are, therefore, as far as we can see at present, and as far as theoretical considerations can aid us, great departures shown by hydrogen from what are fairly general results. Van der Waals's f and Trouton's constant are each only about half the usual values; and we have now found, from the consideration of the point of inversion of the Joule-Thomson effect, and of the product at_c , variations greater than the average from the values we should have expected. Further experiment will be necessary before these discrepancies can be cleared up.

PREPARATION AND PROPERTIES OF PURE COLLOIDAL SILVER.

By A. CHASSEVANT.

IN these new experiments I prepared colloidal silver according to Schneider's method (*Berichte*, vol. xxv., p. 1281) by mixing 500 c.c. of a 10 per cent solution of nitrate of silver, 500 c.c. of a 30 per cent solution of ferrous sulphate, and 700 c.c. of a solution containing 280 grms. of crystallised citrate of soda.

A reddish deposit is obtained, which is separated from its ferruginous mother-liquor, by means of a filter-pump, after having stood for half-an-hour.

The precipitate is re-dissolved in a stream of distilled water, and the solution is treated with about twice its volume of alcohol at 95° . The addition of the alcohol causes a bluish-black deposit to be formed, a precipitate of *sol*. The mixture is filtered through a Chamberland cylinder. The alcoholic solution of ferric citrate traverses the filter, and is collected in a recipient *ad hoc*; the precipitate of colloidal silver is deposited on the outside of the filter in the form of a pasty crust; after some time the filter no longer acts; it is then withdrawn from the liquid, but the aspiration is continued until the crust assumes an iridescent, brilliant metallic appearance, and seems to be dry.

Then placing the filter in a glass containing distilled water the *sol* is allowed to re-dissolve.

I have observed that the Chamberland cylinder, the pores of which are obstructed by the colloidal molecules of silver, acts as a dialyser, and that on adding water and applying the vacuum we can cause the ferric salts and other im-

purities to pass through into the interior, the *sol* of colloidal silver remaining in the outer solution.

The solution may be again precipitated by alcohol at 95° , and again purified, as has just been described. If we have been careful to avoid the presence of all crystalloids, and especially of mineral acids, these operations can be repeated several times, and the colloidal silver retains its properties of a *sol*. Solutions of pure colloidal silver have no longer any tendency to become precipitated as a *gel*. Thus, while in the presence of the mother-liquor during its preparation the black insoluble *gel* is produced in a few hours, solutions of colloidal silver free from electrolytes can be kept for several weeks without any change.

It is interesting, in practice, to notice the action of the alcohol; when we are obliged to leave the colloidal silver in very impure circumstances, it is sufficient to cause the precipitation of the *sol* by means of alcohol; the colloidal silver thus precipitated retains its properties of a colloid for a very long time, even in the presence of an excess of crystalloid salts, which under ordinary circumstances would rapidly transform the colloidal silver into the insoluble *gel*.

By applying this method of purification, I have succeeded in obtaining, after a first purification, a solution of colloidal silver containing per 100 c.c. 0.480 gm. of material dried at 100° , 0.478 gm. of material stable at a bright red heat, and 0.383 gm. of silver, that is 81.7 per cent of silver; the difference was almost entirely iron.

After two purifications, 100 c.c. of the solution contained 0.300 gm. of material dried at 100° , and 0.2897 gm. of silver, or 96.59 per cent of silver.

This pure solution of colloidal silver has all the properties of colloids, which have been published by my friend Posternak and myself, and which have been partly observed by others.

The various electrolytes, dilute carbonate of soda, nitrate of potassium, perchloride of iron, sulphate of copper, &c., cause the precipitation of the *gel*.

If we evaporate the solution *in vacuo*, and dry the pasty mass collected on a Chamberland filter, metallic silver is formed. On the other hand, the aqueous solution of the *sol* is very stable. We can even keep this precipitated *sol* on porcelain in concentrated alcohol. Colloidal silver thus purified dissolves in alcohol, but only in the presence of water; it is insoluble in absolute alcohol. Purified colloidal silver dissolves easily in glycerin at 30° . We obtain organosols observed by Schneider, which will be the subject of a future paper.

If we treat a solution of pure colloidal silver with another colloid, such as gum, gelatin, or a sodic solution of acid-albumose, we can obtain, by evaporating in the cold *in vacuo*, a solid mass in which the silver has preserved its physical colloidal state, and can be re-dissolved in distilled water. I shall return to this in a future paper on these preparations.

The summary of all these facts makes us admit with Carey Lea (*Zeit. Anorg. Chem.* vol. xiv., p. 341) that all the preparations of colloidal silver contain the silver, not in a special allotropic form, but that the fine particles of silver, which were unable to become conglomerated at the moment of their production, have remained in the free state in solution.

The transformation of the *sol* into the *gel*, and into metallic silver, takes place naturally every time the physical molecules are condensed or brought into contact one with the other, either under the influence of electrolytes, by precipitation, by crystallisable salts, or by reason of the loss of liquid support through dilution; by the evaporation of solutions of pure colloidal silver, or by simple mechanical action, as we have shown by grinding up colloidal silver. On the other hand, the colloidal form of silver is stable in pure solution in water, alcohol, or glycerin. In the presence of other colloids we can again conserve silver in the colloidal form, even in the solid state, as shown by Paal (*Berichte*, vol. xxxv., p. 2224), with lylsalbinic acid.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 1.

NEW METHOD FOR THE ESTIMATION OF ORGANIC MATTERS IN WATER, MORE PARTICULARLY IN WATERS CONTAINING CHLORIDES AND BROMIDES.

By C. TENORMAND

WHEN we endeavour to estimate organic matter, by the ordinary methods, in waters containing alkaline chlorides and bromides—such as sea-water, for example,—we obtain results that are necessarily erroneous; in fact, chlorine and bromine are given off as soon as we add the sulphuric acid to the manganic solution, and thus, through this action, the amount of organic matter found is too high.

Among the methods which may be recommended for preventing this error we will describe one which has given us the best results, and which is based on a new adaptation of Duboscq's colorimeter. We have used it for estimating the organic matter in sea-water, and its use can be advantageously extended to the estimation of the organic matter in fresh waters by introducing a modification which we will describe at the end of this paper. We propose to examine successively its technique, its constancy, and its sensitiveness. To begin with, the principle adopted is as follows:—

Boil the water under analysis with a titrated alkaline solution of permanganate of potassium. From this we deduce, by comparison in the colorimeter with the original titrated solution, the amount of permanganate of potash used; that is to say, the quantity of oxygen absorbed by the organic matter.

I. The solutions necessary for the estimation of the organic matter by this new method are—

1. A solution containing 0.395 grm. of permanganate of potassium per litre (10 c.c. of this solution corresponds to 1 m.grm. of oxygen).
2. A saturated solution of bicarbonate of soda.

Place 100 c.c. of the water to be examined in a beaker with 10 c.c. of the permanganate and 10 c.c. of the bicarbonate of soda solutions. Boil for ten minutes, and, after cooling, bring the volume up to 100 c.c. with distilled water. Allow to settle completely, and decant the liquor into one of the colorimeter glasses, and in the other place a solution formed of 10 c.c. of the manganic liquor and 90 c.c. of distilled water. Then make the tints appear equal (see remark at the end of the paper).

Now, let x be the quantity of permanganate remaining after boiling, p the amount of permanganate in 100 c.c. of the check sample, H_1 the degree under which the water in question is being examined, and H that of the check sample. We get—

$$x = p \frac{H_1}{H};$$

or, replacing p by its value,—

$$x = 0.00395 \frac{H_1}{H_1};$$

the amount of permanganate that has disappeared during boiling will be expressed by the formula—

$$0.00395 - 0.00395 \frac{H_1}{H_1} \text{ or } 0.00395 \left(\frac{H_1}{H_1} - \frac{H_1}{H_1} \right),$$

but 0.00395 of permanganate of potassium corresponds to 1 m.grm. of oxygen; the quantity 0.00395 $\left(\frac{H_1}{H_1} - \frac{H_1}{H_1} \right)$ will correspond to a quantity equal to $\frac{H_1 - H_1}{H_1}$.

Example.—Let $H_1 = 40$ and $H = 26.4$, the quantity of oxygen fixed by 100 c.c. of water will be $\frac{40 - 26.4}{40} = 0.34$ m.grm., or 3.4 m.grms. per litre.

II. The method is constant in its applications, and the intensity of the final tint obtained always gives the same results with one particular sample, no matter how many

times it is repeated, provided the operations are conducted under identical conditions.

The following table shows the results obtained in three series of experiments carried out successively on one sample of sea-water diluted with distilled water.

We see that, within one-tenth of a milligram., the results obtained are the same, and that the variations between the three analyses are not greater than two or three hundredths of a milligram. of oxygen on the total amount of organic matter contained in a litre of water.

Dilute Sea Water

H_1	H	$\frac{H_1}{H}$
<i>First Experiment.</i>		
30	23.5	0.216
30	23.7	0.210
30	23.6	0.213
30	23.5	0.216
30	23.7	0.210

Mean 0.213

Oxygen fixed per litre 2.13 m.grms.

Second Experiment.

H_1	H	$\frac{H_1}{H}$
30	23.5	0.216
30	23.6	0.213
30	23.7	0.210
30	23.7	0.210
30	23.6	0.213

Mean 0.212

Oxygen fixed per litre 2.12 m.grms.

Third Experiment.

H_1	H	$\frac{H_1}{H}$
30	23.6	0.213
30	23.4	0.220
30	23.6	0.213
30	23.5	0.216
30	23.5	0.216

Mean 0.215

Oxygen fixed per litre 2.15 m.grms.

III. This method is also very sensitive; its sensitiveness is certainly as great as that of the method in general use for the estimation of organic matter in fresh waters.

In fact, if 10 c.c. of a sample of sea-water we add 2, 4, 6, 8, or 10 c.c. of a solution of peptone containing 0.1 m.grm. of this substance per c.c., we obtain figures between which the differences are practically constant, as will be seen by the following table:—

Peptone added to sample of sea-water.	H_1	H	Differences, in m.m.	Oxygen fixed per litre, in m.grms.	Differences, in m.grms.
0.0	40	29.9		2.525	
0.2	40	26.9	3.0	3.275	0.750
0.4	40	24.0	2.9	4.000	0.725
0.6	40	21.1	2.9	4.725	0.725
0.8	40	18.2	2.9	5.450	0.725
1.0	40	15.2	3.0	6.200	0.750

This table shows further that for a difference of 2.9 m.m. between two successive values of H , there is a difference of 0.725 m.grm., or one thousandth, in the corresponding values of the oxygen absorbed, a variation of $\frac{0.725}{2.9} = 0.25$ m.grm., and for 1/10th of a thousandth, 0.025 m.grm. of oxygen.

Thus an error in reading of $1/10$ th of a m.m. makes a variation in the amount of oxygen of 0.025 m.grm. more or less.

Now, as with a practiced eye the error of reading can be reduced to its minimum by taking the mean of five or six readings, which by the way can be done very rapidly, we can safely say that the error in the determination of the organic matter contained in a litre of water would be at the most 0.05 m.grm. of oxygen; that is to say, a quantity that may be looked upon as insignificant.

Application of this Method to the Estimation of the Organic Matter in Fresh Waters.

In the estimation of the organic matter in sea-water, the clarification of the liquor, before the colorimetric examination, takes place in a few minutes, thanks to the entanglement of the oxide of manganese by the carbonate of magnesium produced during the boiling. With fresh waters, however, this is not the case; the solution maintains for some hours a dull appearance, which renders the colorimetric examination impossible.

But we can make this examination as rapid as that of sea-water by adding, with the other ingredients, 1 c.c. of a saturated solution of sulphate of magnesium; thus the hydrocarbonate of magnesium is formed as in the former case, and the clarification is complete in about ten minutes, or a quarter of an hour at the most.

Remarks.—In practice, and with a view to diminishing the errors of observation, it is as well to examine the waters through as thick a layer as possible. But though it is easy to obtain equality of tints with slightly coloured solutions, the same is not the case when the manganic solution retains almost the whole of its original colour. Under these conditions it is more difficult to arrive at a sensitive tint; but this difficulty can be avoided easily by placing green glasses, with which the apparatus is provided, between the reflecting prisms and the glass cylinders in the slots provided. This new sensitive tint, which is a greenish-yellow, becomes very easy to match.

Finally, we may add that though in particular cases the colour of the check solution is not always absolutely comparable with that of the solution of the water under analysis, it is still easy to make a rigorous comparison. For this purpose we have only to prepare a check solution under the same conditions as that of the water in question, that is to say, boil 100 c.c. of distilled water with 10 c.c. of permanganate of potash, 10 c.c. of bicarbonate of soda, and 1 c.c. of sulphate of magnesia; but the preparation of such a check solution is generally unnecessary, as we have been able to prove.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 15.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION. *Annual Meeting, May 2nd, 1904.*

Sir JAMES CRICHTON-BROWNE, M.D., Treasurer and Vice-President in the Chair.

THE Annual Report of the Committee of Visitors for the year 1903, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read. Seventy new Members were elected in 1903.

Sixty-two Lectures and Twenty Evening Discourses were delivered in 1903. The Books and Pamphlets presented in 1903 amounted to about 229 volumes, making with 694 volumes (including periodicals bound) purchased by the Managers, a total of 923 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—Dr. Henry E. Armstrong, Sir William Abney, Mr. Shelford Bidwell, Sir Alexander Binnie, Mr. J. H. Balfour Browne, K.C., The Hon. Sir Henry Burton Buckley, Sir Thomas A. De la Rue, Bart., Dr. J. A. Fleming, Sir Victor Horsley, Lord Kelvin, Dr. Ludwig Mond, Sir Owen Roberts, Sir Thomas Henry Sanderson, Sir Felix Semon, and Mr. W. H. Spottiswoode.

Visitors—Dr. J. Mitchell Bruce, Mr. J. B. Brown-Morison, Dr. F. Clowes, Dr. Mackenzie Davidson, Mr. W. B. Gibbs, Mr. Francis Fox, Mr. C. E. Melchers, Mr. R. Mond, Mr. J. Callander Ross, The Hon. Walter Rothschild, Mr. Maures Horner, Mr. A. A. Campbell Swinton, Mr. J. J. Vezev, Dr. G. Johnstone Stoney, and Mr. G. P. Willoughby.

CHEMICAL SOCIETY.

Extra Meeting, April 19th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

THIS meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

THE PRESIDENT, in opening the proceedings, said:—So many years have elapsed since we enjoyed the delivery of a Faraday Lecture that perhaps a few words of introduction may not be regarded as inopportune. Faraday died in 1867, and immediately after his decease the Council of the Chemical Society met together and determined that, if possible, they would do something permanently to do honour to his memory; and the result was that, after considerable deliberation, they decided to establish this system of lectures. The first of the course was given in 1869 by Dumas, only two years after Faraday's death. Dumas was succeeded by Cannizzaro, Hofmann, Wurtz, Helmholtz, Mendeleeff, and Lord Rayleigh. You will see, therefore, that the most eminent men of science living at the time were ready to accept the invitation to undertake the office of Faraday Lecturer. Owing to accidental circumstances it is, however, a rather long period—some twenty-three years—since we heard the voice of a Faraday Lecturer. Thanks to the kindness of the Members and the Managers of the Royal Institution, the lectures have all, hitherto, been given within this place, the walls of which for so many years echoed to the voice of Faraday, and which were the witness of his teaching and his triumphs. The Council of the Chemical Society were naturally anxious on the present occasion, as on all previous occasions, to find a man who might safely be regarded as qualified by his own researches and by his own contributions to science, worthily to fill the office of Faraday Lecturer; and they are satisfied that they have found such a man among their own Honorary Members. Professor Ostwald is a man who is not only honoured in the country of his adoption, but is famous throughout the world as the apostle of the modern doctrines concerning chemical affinity and the mechanism of chemical action. I will not, however, occupy any further time, but ask Professor Ostwald to be good enough to give us his lecture.

Prof. OSTWALD then delivered the Faraday Lecture, of which the following account is an abstract:—

Elements and Compounds.

The most general concept underlying all chemical theory is that of a *phase* created by Willard Gibbs. A phase is a physical homogeneous body, which may be either chemi-

cally homogeneous or composed of any number of substances. Every single phase has two degrees of freedom, irrespective of its chemical simplicity or complexity. A difference arises only if a second phase is formed. When that happens, we have two different cases: either the properties of the remaining part of the first phase change during the transformation into a new phase, or they remain constant. Phases of the first order we call *solutions*; of the second, *hydropic bodies*.

By forming a new phase of a solution, we get two portions possessing different properties. On separating these parts, and on repeating the separation into two phases, every solution finally splits up into a finite number of hydropic bodies.

Generally, a hydropic body behaves as such only within certain limits of temperature and pressure. Beyond these limits of stability, it assumes the properties of a solution, and can therefore be split up again into a finite number of other hydropic bodies. These we call *simple bodies* than the former. At last it becomes impossible to change the hydropic body into a solution, because it is not found practicable to reach its limit of stability. *Substances which can form only hydropic phases are called elements*.

With hydropic substances, we can again distinguish two cases. (1) Either the hydropic body can exist as such only at one definite temperature and pressure, and by changing these conditions the body is transformed into a solution. This is the case with solutions of constant boiling-point (for example, the solution of acids investigated by Sir Henry Roscoe) or with cryohydrates, &c. (2) Or there is a finite range of temperatures and pressures within which the phase invariably behaves as a hydropic body; in this case, we have a *substance proper*. A substance or chemical individual is therefore the limiting case of hydropic solutions, and is defined experimentally by its not changing its properties if the phase is partially transformed into another, for example, by distillation or crystallisation. This is indeed the way, in which pure substances are defined and identified practically.

The constancy of properties is casually connected with constancy of composition; that is, if it is possible to produce a substance proper from other substances or hydropic bodies, the ratio of the weights of the component parts must have a certain value in order that this peculiar body of constant proportions may be formed. This is the *law of constant proportions*.

In forming such peculiar bodies, elements and compounds behave alike, and there is, therefore, in every case a certain definite relation between a substance and its components, the last being compounds or elements. A compound substance can therefore be split up into, or regenerated from, elements only in one definite manner. If we form a ternary compound ABC of the elements A, B, and C, we get the same substance by forming first AB and uniting it with C, or by first preparing AC and combining this with B, or, lastly, in forming the compound ABC directly from the elements.

By combining A with B, we get a certain ratio of weights between the two elements, and also a ratio for C by combining it with AB to form ABC. Now, as the composition of ABC is independent of the manner of formation, the composition of a substance AC is not more arbitrary, but is already defined by the composition of ABC, for it must contain A and C in the same ratio as in ABC. In the same way, the composition of a substance BC is defined in such a manner that the elements A, B, C, can combine only in definite ratios, regulated by the combining weight of each element for the compound ABC. This is the *law of combining weights*, generally spoken of as the law of atomic weights.

From this law, the *law of multiple proportions* can be deduced easily by applying the same considerations to the case of two elements forming more than one compound.

All the stoichiometrical laws, which have hitherto been deduced and explained only by the atomic hypothesis, prove to be direct consequences of the purely empirical

definition of the concept of a substance proper or a chemical individual, and the atomic hypothesis is rendered superfluous for the purpose of this deduction.

According to the energetic theory of the elements, these bodies are explained as being distinguishing points of maximum stability relative to all adjacent conceivable substances. If we assume that the two characteristics are sufficient to determine the nature of a substance, and if we put these characteristics in plane co-ordinates horizontally and erect vertical lines in every point of the plane to express the free energy of the corresponding substances, we get a continuous surface like the stalactitic ceiling of a cavern, the end of each stalactite representing an element. A drop of water hanging on the ceiling represents by its flow the possible changes between the elements. To bring the drop from one stalactite to another, it must be raised above the pass between the two stalactites. This requires a certain concentration of free energy, and the practical impossibility of changing one element into another is due to the practical impossibility of bringing about the required concentration of energy. Now, with radium and other unstable elements, energy is not a relative minimum compared with the adjacent possible substances, but only a change in the slope of the surface which represents it. The drop of water can flow of its own accord from the point of the element, and will only lessen its speed on passing through this point. As the drop arrives finally at the end of the stalactite of helium, which is very low indeed (because helium cannot even form compounds), the enormous development of energy connected with this transmutation is explained at once. From the general law, that the most stable point of a changing system is not reached directly, but only through all the possible stages of unstable forms of the system, the intermediate formation of new and transitory substances, and of new and transitory forms of energy is also explained, again without any application of hypothetical atomic concepts.

In presenting the Faraday Medal to Professor Ostwald at the conclusion of the lecture, the PRESIDENT said:—It is now my pleasant duty, Professor Ostwald, in the name of the Society, to offer for your acceptance this medal, which bears the image of Faraday, and which has been struck in commemoration of this occasion.

Prof. DEWAR.—You, Sir, have placed upon me the very onerous duty of expressing the grateful thanks of the members of the Chemical Society of London to Professor Ostwald for the magnificent way in which he has discharged the duties of Faraday Lecturer, and the honour he has done us in accepting that office. You, Sir, have pointed to the great galaxy of talent with which he must be associated for all time, in referring to the great names of those who in the past have occupied the position. Now I am quite sure that every chemist in England, when he heard that Professor Ostwald was selected for this office, had a hopeful anticipation that he would rival his compeers. You, fellow-workers, have listened to the mode in which he has passed through this great ordeal, and I am sure that you will all acknowledge the splendid achievement of his success. I think, Sir, we might even go farther and say that no greater enjoyment could have been given to Faraday, if we could imagine his being present here this evening, than to have received Professor Ostwald; for his life and spirit has been the spirit of Faraday, and that has led to his great position as a worker and to the establishment of his great school of physical chemistry. We may rest assured that the man who has done so much to develop the electro-chemical theory and the theory of dielectrics which originated in this place would have been a delight to Faraday. But I think we ought to go farther, and say that, while in the past we have had the eulogy of Faraday, while we have had admirable summations of his character and work by his admirers, we have never before had such an original pronouncement. We have received for the first time an original contribution that is likely to give us matter for thought for many a day to come. I think that

the selection of the subject of the address in itself would have delighted Faraday, who again and again returned to the discussion of the nature of the elementary bodies. I was curious to ascertain what was the last pronouncement which Faraday gave in this room with regard to the elements; and I found it in a Friday evening lecture in the year 1836 (subsequent to his discovery of definite electrolysis), entitled "The Nature of the Chemical Elements." The last sentence is most interesting. He says:—"Thus, either present elements are the true elements, or else there is the probability before us of obtaining *some more higher and general power of Nature* even than electricity, which at the same time might reveal to us an entirely *new* grade of the elements of matter now hidden from our view and almost from our suspicion." That was Faraday's view sixty-eight years ago, given in this very room and at that very table. It is quite clear that at that time he would have been staggered if he could have known that a substance with which he was familiar, in the form of an oxide, and which had been taken for an element—namely, the substance uranium—contained within itself that very spontaneous change into the "new grade of the elements" which Professor Ostwald has so admirably illustrated.

The Professor's stalactite cavern is a cavern of great mystery, and is indeed one in which we may require a great deal more light before we can get acclimatised to the surroundings. But that does not withdraw one iota from the originality and the brilliancy of the lecture which we have had to-night, and I ask you, Sir, to allow me, on behalf of the Chemical Society and the world of English science, to propose a vote of thanks to Professor Ostwald for the noble way in which he has discharged his duty.

Dr. THORPE—Ladies and Gentlemen, I rise at the bidding of the President to discharge what I feel to be a very honourable duty, namely, to join with Professor Dewar in giving expression to the gratitude which the Fellows of the Chemical Society feel to Professor Ostwald for the Faraday Lecture which he has given to-night. The President has told you that one characteristic of the Faraday Lectures is that they are given in this hall, a hall which, of course, is hallowed by the associations of Faraday. Now, if anybody will cast a retrospective glance over the Faraday Lectures, they will find that there is one fundamental conception common to them all. However different they may seem at first sight, they are all concerned fundamentally with the idea of the essential nature of chemical action and the essential nature of elements and compounds. Now, if those two things be the characteristics, namely, that the Faraday Lectures are given here, and that they are all concerned with that fundamental idea—Professor Dewar would seem to have proved that Faraday himself was the first Faraday Lecturer. I venture, however, to point out that in reality the first Faraday Lecturer was John Dalton, for it was from that very place which Professor Ostwald has just occupied that John Dalton, in the winter of 1809, developed before such an audience as we have here to-night the conceptions which are immortally associated with his name. It was to an audience which, I suppose, may have comprised men like Young, Wollaston, Sir Joseph Banks, and Humphry Davy himself, that John Dalton, in his characteristic, simple, straightforward, lucid way, laid before a Royal Institution audience the first "Faraday Lecture." I have the greatest possible pleasure, Ladies and Gentlemen, in echoing the sentiment which has been so eloquently expressed by my colleague, Professor Dewar, in asking you to tender to Professor Ostwald our most grateful thanks for the intellectual treat which he has afforded us to-night.

LORD RAYLEIGH—I wish the President had seen fit to call upon someone more conversant than I am with the course of chemical thought and speculation to speak to this resolution. I feel that I follow only at a distance, and, although anyone who has heard Professor Ostwald to-night could not fail to take up some valuable ideas, I think most of us must feel that a good deal of thought is required before

we should be in a position to do justice to what has been laid before us. We certainly live in a very interesting time. Twenty or thirty years ago an idea was not uncommon, I think, that we understood tolerably well the general course of Nature, and that all that was wanted was to fill up certain details where difficulties of one sort or another had interfered with our acquiring adequate knowledge. I believe that the feeling at the present day among scientific men, and, perhaps, especially among those scientific men who have taken the largest part in recent work, would be a very much more modest one, and that most of us are quite prepared to recognise that we must face possible revolutions in those ideas which in many cases we have hitherto regarded as most firmly established. It is in connection with such thoughts that I think we recognise the value of what we have heard to-night, and I, certainly, for one shall look forward to studying in detail what has been set before us. I desire most heartily to support the resolution which has been moved and seconded.

The motion was then put by the PRESIDENT and carried with acclamation.

Prof. OSTWALD—Mr. President, Ladies, and Gentlemen, now that my task of reading from print is at an end, I feel a difficulty in going some steps farther into unknown English periods. I cannot bring sufficient English together to express my deep feeling of thanks for the honour which has been shown to me in the way in which you have received my ideas. I feel that I was not mistaken when I tried to bring this work into your own land in the face of one of the best things ever done in science, I mean the atomic hypothesis. My purpose was to show that the atomic hypothesis is no longer necessary to explain the stoichiometrical laws. But the views arrived at, and the progress attained by the use of the atomic hypothesis, cannot be destroyed. They have directed the discoveries of chemistry for a whole century, and if any hypothesis can do good, this one has done so. Therefore I do not think this hypothesis need be interred yet, and when the time comes it should be interred with the greatest honour.

Ordinary Meeting, Wednesday, April 20th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. G. E. P. Broderick, H. W. Gadd, and T. S. Price were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Albert Ernest Bellars, B.A., Magdalene College, Cambridge; Herbert Frank Brand, M.A., B.Sc., 13, Clifton Road, Brockley, S.E.; Thomas Alfred Gerard, 122, Foxhall Road, Nottingham; James Gray Gilchrist, M.A., 48, Ovington Street, Chelsea, S.W.; John Haslam Johnston, M.Sc., Public Offices, Hampton, Middlesex; Alfred Pell, 44, Cumballa Hill, Bombay; David John Pinkerton, 17, Orbiston Street, Motherwell; Percy Richard Sanders, West Cliffe, Seaford, Sussex; James Alfred Wilkinson, M.A., Transvaal Technical Institute, Johannesburg.

The PRESIDENT stated that the Council had resolved to present the following Address to Sir Henry E. Roscoe on the occasion of the celebration of the Jubilee of his Doctorate, on Friday, April 22nd, 1904, fifty years having elapsed since he graduated as Doctor of Philosophy at Heidelberg on March 15th, 1854.

To SIR HENRY ENFIELD ROSCOE, Ph.D., LL.D., D.Sc., F.R.S.

The Officers and Council of the Chemical Society desire to join the rest of your Scientific friends in offering hearty congratulations on the attainment of the Jubilee of your Doctorate.

More than forty years ago, when there were few schools of scientific chemistry in this Country, by your teaching

and example you not only revived the fortunes of the College in Manchester to which, during so many years, you were attached, but assisted in arousing a new spirit in the other teaching institutions of Great Britain.

They recall with pleasure and gratitude the services you rendered to the Society when, many years later, you became its President, and by your genial personal influence assisted so materially in promoting its activity and usefulness.

They wish you many years of health to enjoy the further developments of Scientific Research and the further applications of Scientific Knowledge to useful purposes, to which the greater part of your life has been devoted.

(Signed). WILLIAM A. TILDEN, *President*.
ALEXANDER SCOTT, *Treasurer*.
W. PALMER WYNN } *Secretaries*.
M. O. FORSTER }
WILLIAM RAMSAY, *Foreign Secretary*.

Of the following papers, those marked * were read.

*58. "The Vapour Density of Hydrazine Hydrate." BY ALEXANDER SCOTT.

The determinations by Curtius and Schulz (*Ann. Prakt. Chem.*, 1890, [2], xlii., 529) of the vapour density of hydrazine hydrate at various temperatures are interpreted by them to indicate something quite anomalous in the behaviour of this substance in the state of vapour. They state that at 100° the vapour density determined by Hofmann's method corresponds with the molecule $N_2H_4 \cdot H_2O$, and at 170° at atmospheric pressure to $N_2H_4 + H_2O$, but that at higher temperatures larger molecules are largely regenerated, and that at very high temperatures the vapour density indicates a molecular weight double that of the original. The author finds that at 98.5° the vapour density is 15.8 instead of 25 as required by N_2H_4O , at 138° the dissociation into $N_2H_4 \cdot H_2O$ is complete, and that at higher temperatures a certain amount of decomposition into nitrogen, ammonia, and water occurs. If the vapour densities by V. Meyer's method were determined in an atmosphere of air, oxidation of the hydrazine would ensue, leading to completely erroneous results, even at comparatively low temperatures, but by using nitrogen this source of error is avoided.

*59. "The Combining Volumes of Carbon Monoxide and Oxygen." BY ALEXANDER SCOTT.

The ratio by volume in which carbon monoxide combines with oxygen has been determined by means of the same apparatus as was employed by the author in estimating the composition by volume of water (*Phil. Trans.*, 1893, clxxxiv., A, 543). The results of the author's experiments indicate that the molecular concentration of carbon monoxide is slightly greater than that of oxygen, the combining volumes being $CO : O :: 1.9985 : 1$ with carbon monoxide from calcium oxalate, and $1.9994 : 1$ with that from formic acid. Applying a correction for this to Lord Rayleigh's recently published value for the density of carbon monoxide so as to obtain its molecular weight, we obtain $CO = 27.99$ and $C = 11.99$.

*60. "A Revision of the Atomic Weight of Rubidium." BY EBENEZER HENRY ARCHIBALD.

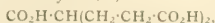
Commercial rubidium iodide was converted into the dichloride ($RbCl_2$) and fractionally crystallised many times until the salt had become spectroscopically free from potassium, when the product was divided into four portions, which each received a different number of additional fractionations. In order to remove the caesium, the rubidium was either repeatedly precipitated as chloride with hydrogen chloride or the hydrogen tartrate was fractionally crystallised. After being fused and bottled by means of Richards's bottling apparatus (*Proc. Am. Acad.*, 1896, xxxi., 55), four samples of rubidium chloride purified by these processes were analysed by precipitating the chlorine with silver nitrate, estimating the amount of silver required for complete precipitation, and also the amount of silver chloride produced. The mean values of the atomic weight of rubidium obtained from 14 analyses were 85.490 and

and 85.484 from the ratios $AgCl : RbCl$ and $Ag : RbCl$ respectively ($O = 16.0$).

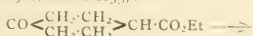
Analysis of rubidium bromide led to the value 85.483, obtained from either of the ratios $AgBr : RbBr$ or $Ag : RbBr$.

*61. "Experiments on the Synthesis of the Terpenes. Part I. Synthesis of Inactive Terpineol, Dipentene, and Terpin Hydrate." BY WILLIAM HENRY PERKIN, jun.

It was recently shown (*Trans.*, 1904, lxxxv., 416) that pentane- $\alpha\gamma$ -tricarboxylic acid,—

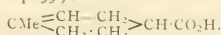


when digested with acetic anhydride and subsequently distilled, is converted into δ -ketohexahydrobenzoic acid. The ester of this acid reacts readily with magnesium methyl iodide, yielding, among other products, *cis*- δ -hydroxyhexahydro- β -toluic acid (compare Stephan and Helle, *Ber.*, 1902, xxxv., 2153):

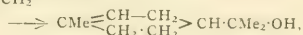
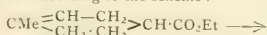


This acid melts at 153°, and on distillation is readily converted into its lactone, a solid, crystalline substance, which melts at 70° and distils at about 185° under 150 m.m. pressure.

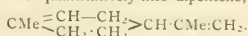
When the hydroxy-acid (or its lactone) is left in contact with fuming aqueous hydrobromic acid it is converted into δ -bromohexahydro- β -toluic acid, a crystalline substance which melts at 126°, and which, when digested with pyridine or with sodium carbonate, yields Δ^8 -tetrahydro- β -toluic acid (m. p. 99°):—



If the ester of this acid is mixed with an excess of an ethereal solution of magnesium methyl iodide, and the product, after remaining for twenty-four hours, is treated with dilute hydrochloric acid, a colourless oil is obtained, which distils at 133° under 60 m.m. pressure, and has a pronounced odour of lilac. That the above reaction takes place according to the scheme:—

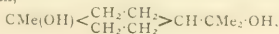


and that the oil obtained is therefore inactive *terpineol* is clearly proved by the following facts. It yielded, on analysis, numbers agreeing with the formula $C_{10}H_{18}O$, and when digested with potassium hydrogen sulphate, was converted almost quantitatively into dipentene,—



The *dipentene* thus synthesised was found to be identical in all respects with that obtained from ordinary *terpineol* by the same process. It distilled at 181–182°, had a characteristic odour of lemons, and yielded with bromine, *dipentenetetra*bromide, $C_{10}H_{16}Br_4$ (m. p. 125°), and, with hydrogen chloride, *dipentene dihydrochloride*, $C_{10}H_{16} \cdot 2HCl$ (m. p. 48–50°).

Furthermore, the synthetical *terpineol* was slowly converted by treatment with dilute sulphuric acid into *terpin hydrate*, $C_{10}H_{18}(OH)_2 \cdot H_2O$ (m. p. 118°), from which *terpin itself*,—



was readily obtained by dehydration.

These experiments are being continued and extended to the study of the behaviour of ethyl γ -ketohexahydrobenzoate and other similarly constituted substances towards magnesium methyl iodide.

*62. "Lævorotatory Modification of Quercitol." BY FREDERICK BELDING POWER and FRANK TUTIN.

Quercitol, $C_6H_{12}O_5$, has hitherto only been found in the

fruits (acorns) of certain species of *Quercus*, in which it exists as a dextrorotatory modification. The levorotatory modification described by the authors was obtained from the leaves of *Gymnocma sylvestre* (Br.), a plant belonging to the family of *Asclepiadaceae*, and indigenous to Banda and the Deccan Peninsula.

l-Quercitol is a colourless, crystalline substance, which, when crystallised from water, has the formula $C_6H_{12}O_6 \cdot H_2O$; it loses its molecule of water at 110° , melts at 174° , and has $[\alpha]_D = 73.9^\circ$. The dried substance separates from ethyl alcohol in the anhydrous state. *Pentaacetyl-l*-quercitol, $C_6H_7(O \cdot C_2H_3O)_5$, crystallises from dilute alcohol in needles, melts at $124-125^\circ$, and has $[\alpha]_D = 26.0^\circ$. *Pentabenzoyl-l*-quercitol, $C_6H_7(O \cdot C_7H_5O)_5$, separates from a mixture of alcohol, ethyl acetate, and petroleum in needles containing a molecule of alcohol, which, when heated slowly, melt at 148° ; it has $[\alpha]_D = 79.0^\circ$. On oxidising *l*-quercitol with sodium hypobromite and treating the product with phenylhydrazine, *dibromodihydroxyhexahydrobenzocyclohexadiene*, $C_6H_3(OH)_3(N \cdot NH \cdot C_6H_5)_2$, was obtained, which separates from alcohol in yellow needles and melts at 209° . On oxidising with cold potassium permanganate solution, malonic acid was obtained, and was identified by means of its ethyl ester.

Kiliani and Schaefer (*Ber.*, 1896, xxix, 1762) have shown that *d*-quercitol is a pentahydroxyhexahydrobenzene, by the formation, on the one hand, of malonic acid, and, on the other, of a diketone, $C_6H_8O_5$. The substance isolated by the authors, designated as *l*-quercitol, is, therefore, one of the eight possible isomerides of pentahydroxyhexahydrobenzene, but, until a further number of these have been isolated, it will be impossible to assign to either of the known quercitols a definite configuration.

*63. "The Constituents of the Essential Oil of Californian Laurel." By FREDERICK BELDING POWER and FREDERICK HERBERT LEES.

The Californian laurel, *Umbellularia Californica* (Nuttall), a handsome evergreen tree, occurring in California and Oregon, is also known as "mountain laurel," "cageput," "spice tree," "California olive," "California bay tree," and "pepper-wood."

The essential oil of the leaves had a pale yellow colour and an odour which was at first agreeably aromatic, but when more strongly inhaled became exceedingly irritating to the mucous membranes of the nose and eyes, producing the effects that have previously been described. The oil had a sp. gr. 0.9483 at $16^\circ/16^\circ$, and $[\alpha]_D = 22^\circ$ in a 100 m.m. tube; it was completely soluble in 1.5 parts of 70 per cent alcohol. It was found to contain an inappreciable amount of esters and a very small quantity of a mixture of free fatty acids, including formic acid. The essential constituents of the oil were found to be: eugenol, *l*-pinene, cineol, safrole, eugenol methyl ether, veratrilic acid, and a new, unsaturated, cyclic ketone, *umbellulone*, $C_{10}H_{14}O$, which is a colourless liquid with a somewhat mint-like odour, having in a high degree the peculiar pungency of the original oil. It boils at $219-220^\circ$ (corr.), has a sp. gr. of 0.9581 at $15^\circ/15^\circ$, and $[\alpha]_D = 37^\circ$. This ketone does not react normally with semicarbazide and hydroxylamine, affording with the former, *semicarbazodihydro-umbellulonesemicarbazone*,



(m.p. 217°), and with the latter, *hydroxylaminodihydro-umbellulonesoxime*, $C_{10}H_{15}(NOH) \cdot NH \cdot OH$ (compare *Ber.*, 1897, xxx., 230, 251; 1900, xxxiii, 562; and 1903, xxxvi., 4377).

The relative proportions of these constituents of the oil were approximately as follows:—Umbellulone, 60; cineol, 20; eugenol methyl ether, 10; pinene, 6, and eugenol, 1.7 per cent respectively, together with a very small amount of safrole.

*64. "Some Derivatives of Umbellulone." By FREDERICK HERBERT LEES.

With the view of elucidating the constitution of um-

bellulone, $C_{10}H_{14}O$, the new ketone isolated by Power and the author from the essential oil of Californian laurel, the following derivatives have been prepared.

Umbellulone combines directly in the cold with only 2 atomic proportions of bromine, forming *umbellulone dibromide*, $C_{10}H_{12}OBr_2$, an unstable oil. Umbellulone would therefore appear to contain only one ethylenic linking, and in consideration of this circumstance and the fact that, like the $\alpha\beta$ -unsaturated ketones generally, it behaves abnormally towards hydroxylamine and semicarbazide, one molecule of the ketone interacting with two molecules of these bases respectively (compare preceding abstract), it is regarded as an $\alpha\delta$ -unsaturated cyclic ketone containing two closed rings.

When umbellulone dibromide is heated under diminished pressure, it loses hydrogen bromide, yielding an *unsaturated bromo-ketone*, $C_{10}H_{13}OBr$ (b. p. $140-145^\circ$ 20 m.m.), and *dibromodihydroumbellulone*, $C_{10}H_{14}OBr_2$, which forms needles melting at $119-119.5^\circ$ and having $[\alpha]_D + 6.4^\circ$ in chloroform. When the unsaturated bromo-ketone is reduced with zinc dust and acetic acid, a *saturated ketone* $C_{10}H_{16}O$ (b. p. $214-217^\circ$) is produced; it is the *semicarbazone* of the latter, $C_{10}H_{16}N \cdot NH \cdot CO \cdot NH_2$, forms needles which melt at $171-172^\circ$.

When *dibromodihydroumbellulone* is reduced with zinc dust and acetic acid, it is converted into *bromodihydroumbellulone*, $C_{10}H_{15}OBr$, which forms needles melting at $58-59^\circ$ and having $[\alpha]_D 70.1^\circ$ in chloroform. When this bromo-derivative is reduced with sodium and alcohol, it gives *tetrahydroumbellulol*, $C_{10}H_{19}OH$ (b. p. $207-208^\circ/760$ m.m.), which has a sp. gr. 0.9071 at $15^\circ/15^\circ$ and $[\alpha]_D + 6.6^\circ$.

Umbellulone is easily oxidised by cold potassium permanganate, yielding a *lactone*, $C_9H_{12}O_2$, together with several acids which have not yet been investigated.

The author wishes to reserve the further investigation of umbellulone.

(To be continued).

Conditions of Formation and the Solubility of Cuprosodic Sulphate.—J. Koppel.—Nassol and Maldés (*Comptes Rendus*, vol. cxxxiii., p. 287), in their researches on the solubility of mixtures of sulphate of copper and sulphate of soda, observed that at a low temperature the composition of a solution doubly saturated with regard to the two salts is independent of the ratio of the masses of the two salts present; but that as soon as the temperature is sufficient for the anhydrous modification of sulphate of soda to take rise (from 23° to 32° , according to the mixture), the composition of the solution varies with the relative proportions of the two salts used. Now, the phase rule teaches us that such a result can only be observed in the case where the two salts give place to either isomorphous mixtures or to a double salt. As there is no question of isomorphism between $SO_4Cu_5H_2O$, which is triclinic, $SO_4Na_2 \cdot 10H_2O$, which is clinorhombic, and SO_4Na_2 , which is orthorhombic, the observations of Nassol and Maldés point to the existence of a double salt. This double salt being apparently formed, with a loss of water, from two hydrated salts, it follows from a law given by van't Hoff (*Bull. Soc. Chim.*, vol. xxviii., p. 218) that its production should be brought about by a rise of temperature. The author has succeeded in isolating this double salt, which corresponds to the formula $SO_4Na_2 \cdot SO_4Cu_2 \cdot 2H_2O$; the thermometric and dilatometric examination of its formation and of its decomposition shows that its transformation point is 16.7° . This salt is identical with a natural mineral, *kr hnikite*. The author has determined its solubility, both in pure water and in solutions of one or the other of the two component salts. The results obtained below the transformation point agree with those obtained by Nassol and Maldés; those obtained above this point are decidedly different, these chemists having operated on mixtures in course of transformation without waiting until equilibrium had been reached.—*Zeit. Physik. Chem.*, vol. xlii., p. 1.

NOTICES OF BOOKS

Entropy. By JAMES SWINBURNE. London: A. Constable and Co., Limited. Pp. 137.

In his preface the author states that his reason for writing this book is that it is very much wanted, as there is no work in English, so far as he is aware, that gives a correct definition of entropy. In his first chapter he says:—"Most writers, after defining entropy incorrectly, unconsciously depart from their definitions in dealing with the $\theta\phi$ diagram, so that the two errors approximately cancel out." This possibly accounts for our own unfortunate condition, in which, however, we happen to know that we are not unique, for before reading this book we were quite ignorant of what entropy is; nor, to be candid, are we quite certain that we are much wiser now.

On page 8 we read:—"Entropy may be defined thus—Increase of entropy is a quantity which, when multiplied by the lowest available temperature, gives the incurred waste."

Strictly speaking, this is not a definition of entropy; but if we interpret the statement correctly, it supplies data by which a definite idea of the nature of entropy may be obtained, and also supplies the means by which its exact quantity with certain restrictions may be calculated in terms of known physical units.

On page 105 we find the following statement:—"It may seem strange that a standard state has to be taken for zero entropy instead of simply finding the total entropy of a body and stating it. The usual reason given is that the total entropy of a body is unknown. The real reason is that the entropy of a body is necessarily infinite. If a body of unit mass is imagined at zero temperature, that is taken as zero entropy, because as no heat can be given out no further reduction of θ is possible, to heat it up to any finite temperature θ , the increase of entropy necessarily is—

$$\int_0^\infty \frac{d\theta}{\theta} = \phi,$$

so—

$$\phi = \log \theta_1 - \log \theta_0;$$

but $\log \theta_0$ or $\log 0$ is negative infinity, so the entropy needed to raise the body to any finite temperature is infinite."

This is a surprising statement, and one which we find hard to reconcile with the so-called definition of entropy on page 8. For consider the equation—

$$\int \frac{d\theta}{\theta} = \phi;$$

if this means anything, it means—

$$\theta d\phi = d\theta.$$

and put into ordinary language it reads:—"Increase of entropy multiplied by the temperature equals the increase of temperature; whence it apparently follows that "increase of temperature" is "incurred waste," but it seems safer to conclude that the author's two statements are inconsistent. Moreover, we fail to equate either of them with the statement made by M. Berthelot:—"For example, entropy being represented by $\int \frac{dQ}{T}$, one has $dQ = c dT$; c being the specific heat, which is itself a function of T ."

M. Berthelot, writing in French, escapes the sweeping condemnation of English works referred to above. If his statement be correct, it follows that the author's are wrong, unless it be conceded that—

$$\text{"Incurred waste"} = dQ.$$

To return to page 105. We see no reason to doubt the usual reason given for not stating the total entropy of a body; it is at present unknown, because the physical constants have not been determined for the whole scale of temperatures. As for the statement that the entropy is

infinite, we see no justification; it may be true; if so, it is surprising.

When we come to the use made of the $\theta\phi$ (or entropy) diagram, the author writes on more conventional lines, and as he justly remarks, more use might be made of this method of localising and checking waste of heat. The repetition of the diagrams from page to page, so long as the discussion on them lasts, is very convenient.

The Old Riddle and the Newest Answer. By JOHN GERARD, S.J., F.L.S. London, New York, and Bombay: Longmans, Green, and Co. 1904.

In the preface to this volume it is stated that it aims at investigating the assumption on the part of Science that she has solved the riddle of Nature. The first part examines the truth of the law of evolution, using the term in its widest sense, and criticises Prof. Haeckel's "Riddle of the Universe." Here our author shows himself, it must be admitted, skilful in argument and judicious in the conclusions he draws, and undoubtedly there are to be found scientific men who will, in part at any rate, agree with his deductions, though they might not altogether approve of his methods. In the second part he deals with the principle of evolution as applied to organic nature only and with the Darwinian theory of natural selection. But he does not seem to realise that the fact that Darwin made some mistakes does not disprove his whole theory, and isolated quotations from various authors' works as given in this book cannot be taken in any sense as authoritative. And a serious defect in our author's method appears to be the way in which he would lead an uninformed reader to infer that Darwin himself had not realised the weakness in the demonstrative proof of his theory, and explained this weakness in detail in the chapter in the "Origin of Species" on the "Imperfection of the Geological Record." Whether Darwin's answer to these objections, which he himself actually suggested in many instances, is satisfactory, is a question for individual decision, but the matter will take a different aspect in the minds of many if they first read the chapter referred to in the "Origin of Species."

At any rate it may be affirmed that on the whole the author displays an earnest spirit of enquiry and no little skill in the use of the material he has collected.

Die Elektrolytische Refinement des Kupfers. ("The Electrolytic Refining of Copper"). By TITUS ULKE, M.E. Translated into German by VIKTOR ENGELHARDT. Halle-a-S.: Wilhelm Knapp. 1904.

THE author of this monograph has had many opportunities of personally visiting some of the most important works in which copper ores are treated by electrolytic means, and has thus made himself acquainted with much interesting and useful information concerning output and arrangement of plant. He has also collected accurate information with regard to so-called secret methods, and has carefully abstracted French, German, English, and American patent literature. Thus the book, which contains several valuable plans, will be found very useful by works managers and others.

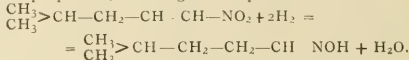
The translator has been confronted with a difficulty in performing his task as regards the conversion of the various numbers given into the metric system. After considering the various courses open to him, he has decided to retain the numbers as given in the text, and adds in brackets the values in round numbers in the metric system.

Classification des Corps Simples. ("The Classification of Elementary Substances"). By M. HENRI MOISSAN. Paris: Masson et Cie. 1904.

IN this extract from the "Traité de Chimie Minérale," after discussing shortly the definition and nature of an elementary substance, the author proceeds to give a brief historical

account of the theories which have been put forward regarding the classification of the elements from the earliest times up to the present day. The various systems of Thénard, Berzelius, Frémy, Naquet, Mendeleef, and Lothar Meyer are then explained, and the author's suggestions put forward for grouping the elements into natural families, taking into account their physical and chemical properties. The differences between his and other systems of classification are clearly explained, while the difficulties of a satisfactory solution of the problem are fully recognised.

with ether and distilled *in vacuo*; it consists of nitroisohexylene. It can be reduced by aluminium amalgam or zinc powder and acetic acid, with the formation of isobutyl-acetaldoxime. Thus the reduction of the nitrated derivative of the non-saturated carbide has given the oxime as a unique product, according to the equation—



CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 14, April 5, 1904.

This issue contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 13.

Alloys of Copper and Magnesium.—O. Boudouard.—Already noticed.

The Electrolytic Estimation of Small Quantities of Silver in the presence of a large Amount of Lead.—MM. Arth and Nicolas.—Already inserted in full.

The Volumetric Estimation of the Alkaline Nitroprussiates and of the Soluble Salts of Cadmium.—MM. Fonze-Diacon and Carquet.—Already inserted.

The Toxicity of Nitroprussiate of Soda.—MM. Fonze-Diacon and Carquet.—A mean dose of 0.25 gm. of nitroprussiate of soda, per kilogram of the animal, will kill a rabbit, either when administered by the mouth or by hypodermic injection. In this way it may be calculated that for an ordinary man of 150 lbs. weight, 17 or 18 grms. of nitroprussiate of soda would be fatal. A post mortem examination shows the presence of hydrocyanic acid in the stomach. It is probable that the nitroprussiate of soda in the presence of the lactic acid in the stomach is decomposed by the gastric glands, as is chloride of sodium; thus an unstable body is formed which would give rise to the formation of prussic acid.

The Degree of Accuracy attained in the Detection of Traces of Arsenic in Organic Matters.—Armand Gautier.—A reply to criticisms of his method. The author points out that he can recover arsenic integrally, even when dealing with such minute quantities as one or two thousandths of a m.-gm. in 50 million times its weight of organic matter.

A Method for the Gradual Synthesis of the Fatty Aldehydes.—MM. L. Bouveault and A. Wahl.—An equimolecular mixture of nitromethane and valeral is placed in a flask, and 1 molecule of 30 per cent aqueous caustic potash added a little at a time. The temperature must be kept down to 30°. When all the potash has been added the solution becomes yellow, and is then poured into an excess of dilute hydrochloric acid; an oil is precipitated, which is extracted with ether and distilled. The nitrated alcohol is a pale liquid, boiling at 110° under 15 m.m., but it is not necessary to distil *in vacuo* before transforming in nitroisohexylene, the raw product being sufficiently pure to be treated at once. To effect the dehydration, the product is dissolved in five times its weight of glacial acetic acid in which a quantity of fused chloride of zinc has been already dissolved, equal to half the weight of the nitrated alcohol to be treated; then boil with a vertical condenser for five or six hours. The liquid is then distilled with steam, and the portion floating on the distillate is collected

A Series of New Acids with an Acetylenic Function.—Ch. Moureu and R. Delange.—Already noticed.

The Hydration of the Acetylenic Acids. Synthesis of Caprylic and Pelargonic Acids.—Ch. Moureu and R. Delange.—The acetylenic acids, $\text{R}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$, are capable of fixing four atoms of hydrogen by the opening of the triple bond, giving the corresponding saturated acids, $\text{R}-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{H}$. This has been specially done with the two natural fatty acids: caprylic acid, $\text{CH}_3-(\text{CH}_2)_6-\text{CO}_2\text{H}$, which exists in the form of a glyceride in certain natural fatty bodies, particularly in butter, by starting with amylpropionic acid, $\text{CH}_3(\text{CH}_2)_4-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$; and with pelargonic acid, $\text{CH}_3(\text{CH}_2)_7-\text{CO}_2\text{H}$, starting with hexylpropionic acid, $\text{CH}_3(\text{CH}_2)_5-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$.

A New Fatty Acid, $\gamma, \gamma', \gamma''$ -Trimethylbutyric Acid.—Ch. Moureu and R. Delange.—Dissolve 14.20 grms. (1 molecule) of trimethyltetrolic acid in 1000 grms. of absolute alcohol, and gradually add 100 grms. of sodium to the boiling solution. Heat with a vertical condenser until all the sodium has reacted. Distil off the excess of alcohol, completing the operation *in vacuo*, and throw the dry residue, a little at a time, into 1000 c.c. of water. The alcohol formed by the decomposition of the alkaline ethylate is separated by distillation, and the aqueous residue cooled. This is carefully treated with a slight excess of dilute sulphuric acid, causing an oily appearance. The mixture is exhausted with ether, and the ethereal solution washed first with a concentrated aqueous solution of chloride of calcium, then with water; dry over anhydrous sulphate of soda, evaporate the ether, and rectify the residue at atmospheric pressure. This new acid congeals almost instantly in a freezing mixture, and by spontaneous heating it melts between -1° and $+3^\circ$. Its density at 20° is 0.9129, and at 0° in the superfluid state 0.9238.

The Hydration of Acids with an Acetylenic Function. New Method for the Synthesis of the Non-substituted β -Ketonic Acids and Ethers.—Ch. Moureu and R. Delange.—Already noticed.

The Decomposition of the Acetylenic Acids by the Alkalis.—Ch. Moureu and R. Delange.—When we prepare the non-substituted β -ketonic acids, $\text{R}-\text{CO}-\text{CH}_2-\text{CO}_2\text{H}$, by heating the acetylenic acids, $\text{R}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$, with a caustic alkali in alcoholic solution, we always observe the production of a certain quantity of the corresponding acetone, $\text{R}-\text{CO}-\text{CH}_3$. This is formed by the normal decomposition of the β -ketonic acid, which is formed according to the equation—



This acetone is found in solution in the ether with which we shake the alkaline liquor, resulting from the addition of an excess of water to the alcoholic mixture, as soon as the reaction is terminated. It is isolated by distillation. The author then goes on to describe in detail the method of treating several acetylenic acids in this manner, such as propylpropionic, amylpropionic, isopropylpropionic, and other acids.

General Observations on the Acetylenic Acids, $\text{R}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$.—Ch. Moureu and R. Delange.—The authors point out the close relationship between the acetylenic acids and the non-substituted β -ketonic acids.

The Amylchloracrylic Ethers.—Ch. Moureu and R. Delange.—A solution of 10 grms. of amylpropionic acid

in 50 grms. of absolute alcohol is saturated at 0° with a current of dry hydrochloric acid gas. After twenty-four hours the mixture is thrown into an excess of water, the whole shaken up with ether, the ethereal layer washed with water, dried over anhydrous sulphate of soda, and distilled. Thus 11.5 grms. of a colourless oil are collected which has the same proportion of chlorine as amylchlorate of ethyl, $C_5H_{11}Cl-C_2H_5Cl-CO_2C_2H_5$. The authors show that the chlorine must be in the 8 position with regard to the carboxethyl in their amylchloracrylic ether.

The Nitric Ethers of the Acid Alcohols.—H. Duval. —The author has shown that the analysis of raw nitrate of glycolic acid gives too high a figure for the carbon; as the water was correct, he considered that there must be another product formed richer in carbon, resulting from a condensation of the glycolic acid; he also showed that there was an oil deposited during the crystallisation of the nitrate of glycolic acid. The examination of this oily compound led him to admit the formation of nitrate of acetoxyacetic acid answering to the formula $CH_3O.NO_2-COOCH_2-CO_2H$, which is the nitrate of the ether obtained by the elimination of a molecule of water between the alcohol and the acid formations of the two molecules of glycolic acid.

The Action of Hydrated Oxide of Bismuth on the Acid Isomers of Gallic Acid, and its combination with Pyrogallalcarbonic Acid.—Paul Thibault. —Bismuthopyrogallalcarbonic acid was prepared by reacting in the cold with an excess of pyrogallalcarbonic acid on pure gelatinous oxide of bismuth in the presence of water; after contact for ten days in a sealed tube, it was opened, decanted, and washed with cold water, or better still with alcohol, after making sure that the pyrogallalcarbonic acid is in excess; dry *in vacuo* over sulphuric acid, or in the oven. Analysis shows the formula to be $C_7H_5O_6Bi$. It is a golden yellow powder, crystallised in needle-like prisms, soluble in strong acids and caustic alkalis, insoluble in acetic acid, even when boiling, and in the neutral solvents such as alcohol, ether, chloroform, &c. It decomposes at about 195–200°, and its density at 18° is 3.51.

Tetraphenylbutanediol and its Products of Dehydration.—Armand Valeur. —Already noticed.

The Action of Sulphur on the Organo-magnesian Compounds.—Henri Wuyts and G. Cosyns. —The author describes the action of sulphur on ethylidide of magnesium, and on phenylbromide of magnesium; he also describes a method for the preparation of thiophenol by the reduction of disulphide of phenyl.

Influence of its Surroundings on Vegetable Acidity.—E. Charabot and A. H-bert. —In the young plant the acid of the leaves and stem is more alkaline than that of the roots; as the plant develops the alkalinity decreases in the former and increases in the latter, which finally becomes the most alkaline of the two. In fact, the mineral salts increase the proportion of combined acids in the aerial portion of the plant.

F. Soddy, M.A., entitled "Radio-Activity: an Elementary Treatise from the Standpoint of the Disintegration Theory." This is intended as a text-book for students and others interested in the fascinating research work connected with Radium and other radio-active substances. The same Company will issue in a few days a book by Prof. S. Lemström entitled "Electricity Applied to Agriculture and Horticulture." In this work Prof. Lemström describes the results of a number of important experiments in England, France, Finland, and Sweden on the value to the cultivator of the electric current in accelerating the growth, improving the quality, and increasing the yield of farm, orchard, market garden, and glasshouse crops.

MEETINGS FOR THE WEEK.

- MONDAY, 9th.—Royal Institution, 5. General Monthly Meeting. Society of Arts, 4.30. (Cantor Lectures), "The Majolica and Glazed Earthenware of Tuscany," by Prof. R. Langton Douglas, M.A.
- TUESDAY, 10th.—Royal Institution, 5. "Meteorites," by L. Fletcher, F.R.S., &c. Society of Arts, 8. "Crystalline Glazes and their Application to the Decoration of Pottery," by William Burton, F.C.S.
- WEDNESDAY, 11th.—Society of Arts, 8. "Early Painting in Miniature," by Richard R. Holmes, C.V.O.
- THURSDAY, 12th.—Royal Institution, 5. "Great Britain and Europe (1763–1793)," by Arthur Hassall, M.A. Society of Arts, 4.30. "British Grown Tea," by A. G. Stanton.
- FRIDAY, 13th.—Royal Institution, 9. "The Queen Victoria Memorial," by M. H. Spielmann, F.S.A.
- SATURDAY, 14th.—Royal Institution, 3. "Sonata Style and the Sonata Forms" (with Musical Illustrations), by Donald Francis Tovey, B.A.

Chemist required immediately for an Explosives Factory. One with knowledge of Nitro-glycerin and Cordite preferred. State salary required and give references.—Address, "Chemist," care of Street's, 30, Cornhill, London, E.C.

Completely equipped and well-lighted Chemical and Assay Laboratory FOR SALE. Near Mansion House station, E.C. Present connection can be transferred to purchaser. Good opportunity for establishing or enlarging practice.—A dress, "Alpha," care of J. W. Vickers, 5, Nicholas Lane, London, E.C.

Director required to invest £5000 to £7000 in a large Chemical Manure Manufacturing Business on an extensive scale. Security certain. Reason of requirement, death of former Director.—Write to K. B., care of Gould's Advertising Agency, 54, New Oxford Street, London, W.

Wanted in an Ammunition Works near London, a Young Man with a knowledge of Chemistry, to assist in the Laboratory and in other scientific and practical work connected with the factory. An exceptional opportunity to gain a thorough knowledge of manufacture and explosives.—Apply, by letter only, with testimonials, to "Ammunition," 16, Great George Street, Westminster.

UNIVERSITY OF BIRMINGHAM.

FACULTY OF SCIENCE.

RESEARCH SCHOLARSHIPS.

Each of the value of about £50 (founded by the late T. AUBREY BOWEN Esq., of Melbourne, Australia).

- Two BOWEN SCHOLARSHIPS in ENGINEERING.
- One BOWEN SCHOLARSHIP in ALLIED SCIENCES.
- Three PRIESTLEY SCHOLARSHIPS in CHEMISTRY.

The object of these Scholarships is to encourage higher work and research in Scientific Professional Engineering and in Chemical and Metallurgical Science. Applications, supported by details of educational training, and references to former teachers and others, should be sent to the REGISTRAR on or before June 1st, 1904.

The Scholarships will be tenable during the Session 1904–5. Further particulars may be obtained on application to the REGISTRAR.

MISCELLANEOUS.

South-Western Polytechnic, Chelsea.—Earl Cadogan, K.G., presents the Prizes and Certificates to Students of Evening Classes and Day Colleges for Men and Women to-day, at 8 p.m. On Saturday, May 7th, at 7 p.m., a Conversation will be held, including scientific lectures and demonstrations, exhibits in Science, Art, and Domestic Economy, gymnastic displays, and musical entertainments. The laboratories and workshops will be open for inspection. Admission by ticket.

Forthcoming Books.—The Electrician Printing and Publishing Co., Salisbury Court, London, announce that they will issue early in May an important work by Mr.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

Founded 1877. Incorporated by Royal Charter 1885.

INTERMEDIATE AND FINAL EXAMINATIONS will be held at the Laboratories of the Institute, commencing on **TUESDAY**, the 5th day of **JULY**, 1904. The Examinations will be open only to Candidates who have complied with the Regulations. Applications must be forwarded not later than **TUESDAY**, the 7th day of **JUNE**, on which day the List of Candidates for the July Examinations will be closed.—For further particulars apply to the **REGISTRAR**, 30, Bloomsbury Square, London, W.C.

UNIVERSITY OF BIRMINGHAM.

DEPARTMENT OF METALLURGY.

Applications are invited for the Post of **ASSISTANT LECTURER AND DEMONSTRATOR IN METALLURGY**. Stipend £150 per annum. The successful Candidate will be required to commence work on the 1st of September next, to devote his whole time to the duties of the office, and to work under and carry out the instructions of the Professor of Metallurgy. Applications, accompanied by copies of three recent testimonials, should be forwarded to the undersigned on or before **Tuesday, May 31st**.

Further particulars may be obtained from—
GEO. H. MORLEY,
Secretary.

E. GEORGE & SONS, BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.

Are OPEN to PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application

BRYAN CORCORAN LIM.

MILLSTONE BUILDERS,

WIRE WEAVERS, MACHINE MANUFACTURERS, AND
GENERAL MILL FURNISHERS.

Sole Makers of MILBURN'S

Patent Conoidal Stone Grinding Mills.

Especially suitable for certain materials, Wet or Dry

Works and Warehouses: Back Church Lane.

Parcel Dept.: Basement of the Corp Exchange

31, MARK LANE, LONDON.



OLD PLATINUM

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver
Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and Purchased.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC,
As described in the "Report of the Inland Revenue Departmental
Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET
LEAD and PIPE, LITHARGE, &c.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.

LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.

RADIUM

ON SALE AND LET ON HIRE.—Write for terms

The following can be had by return of post.

Pitchblende, direct from Joachimsthal, very radio-active, from 1 lb. to 30 lb. per piece.

It also nite, or flexible sandstone, 10 to 25 lb. per piece (very rare).

Kunzite, 1 lb. per gramme. Selected, clear, 2/-

Spartzite (see NATURE, 31/3 04, fol. 523), 2/- and upwards.

Chlorophane, 2/- and upwards Barium Platino Cyanide in large

Crystals in course of manufacture. (ORDERS BOOKED).

Zinc Sulphide. Phosphorescing a beautiful Green, 2/6 per tube.

" " " " Yellow, 2/6 "

Calcium Sulphide " " Violet, 1/- "

Radio-active Residue from which Radium is made; very scarce, 2 lb. tube.

Potassium Sulphide, in tubes of one gramme, 21/-

" on Bismuth Rod or Disc, ... 25/-

" on Copper " " 25/-

Radio-active Screens (Willemite), 6d. per sq. inch. Plat. Bar.

" (Zinc Sulphide), 9d. sq. inch.

" " (Zinc Sulphide), 2 x 10 cm. 7/6.

Professional Men, Universities, Schools, &c., allowed special terms

Our newly invented Thorium Inhalers may be had on hire.

ARMBRECHT, NELSON & CO.,
71 & 73 DUKE ST., GROSVENOR SQ., LONDON, W.

Telephone: GERRARD 4942.

N.B.—We have to day received a consignment of the New Zealand Vegetable Caterpillar; it is from 2 to 3 inches long, with a stem showing true indication growing out of its head. Scientific name of the insect is *Heliothis virescens*; the name of the fungus is *Sphaeria Robertiana*. Specimens may be had from 10/6 to 2/1 according to quality and size.

TERMS CASH WITH ORDER.

Goods may be returned if not approved of, when money will be refunded.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly
Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered
at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

THE CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post
free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 10 words to line)	0	3	6
Each additional line	..	..	0 0 6
Whole column	..	..	1 15 0
Whole page	..	..	3 0 0

A reduction made for a series of insertions.

Cheques and Post Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2320.

THE VOLUMETRIC ESTIMATION OF CYANOGEN.

By JOHN M. DOWALL,
Chemist to the Bakers and Confectioners Co., Ltd., Peterborough.

When the blue solution, produced by adding ammonia to a cupric salt, is added to potassium cyanide, the colour disappears until a certain quantity of the coloured solution has been added; then it ceases to be decolourised. On account of the intense colour it seemed that it would make a good standard solution for volumetrically determining the amount of cyanogen present in the presence of chlorides.

The standard solution was made by dissolving 25 grms. of copper sulphate and pouring the solution into a litre flask, then adding distilled water till the flask was half filled; ammonia was then added till a clear blue liquid was produced; the liquid was then diluted up to the mark. The solution was standardised by weighing out 0.5 gm. chemically pure potassium cyanide, dissolving in 100 c.c. water, and adding 5 c.c. of ammonia. The blue solution was then run in with constant stirring until the colour began to disappear slowly, and then drop by drop. The finish is very sharp, one drop being sufficient to tinge the solution a light blue colour, very conspicuous against a white tile.

The following experiments were made to see if chloride had any action. Three beakers were marked respectively I., II., III. Into I. 1 gm. sodium chloride, 2 grms. were added to II., 3 grms. to III.; weighed quantities of cyanide were also added, and 100 c.c. water and 5 c.c. ammonia to each beaker. The result was as follows:—

No.	KCN added. Gm.	KCN found. Gm.
I.	1.5	1.5
II.	0.98	0.96
III.	0.64	0.64

This method is therefore as accurate, as the silver assay and chloride do not interfere. It has the advantage over the silver method of not being acted on by light, and is much cheaper, a matter of some importance where many assays of cyanides have to be done daily. It has also a coloured finish, which is preferable to turbidity in volumetric work. It will be useful in mining districts as a speedy and accurate method for determining the purity of the potassium cyanide used for the extraction of gold.

THE DETECTION OF CHLORIDES IN THE PRESENCE OF BROMIDES.

By CHAPMAN JONES, F.I.C., F.C.S., &c.

The only difficulty concerning halogen salts in general qualitative analysis is the detection of a small quantity of a chloride in the presence of a bromide. The methods suggested consist, as a rule, either in eliminating the bromine and then testing for the chlorine, or in precipitating both as silver salts and dissolving out the silver chloride. In the first case the separation is rarely if ever sharp, either a little bromine is left behind or a little chlorine is lost, and it is therefore impossible to say whether or not a little chlorine is present. In the other method there is no loss, and this is a very considerable advantage, but in both the presence and the absence of a little chlorine a positive result is generally obtained, and it remains to discover whether a slight turbidity, produced on re-precipitation from the extract, is due to silver chloride or bromide. With suffi-

cient practice and care this is not impossible when using the reagents that have already been proposed, but a more distinct difference between the two salts is very desirable.

During the last year or two I have used ammonium bicarbonate for this purpose with much satisfaction. A saturated aqueous solution of this salt has the advantage that it is more definite than a dilute solution of ammonia or a solution of any other carbonate of ammonia, and also that it shows a greater difference in its behaviour to the two silver salts. Mr. R. H. Beckett, B.Sc., of this College, has carefully confirmed the following statements, using the precipitated silver salts in as nearly as possible the condition in which they generally occur.

If a cold saturated solution of ammonium bicarbonate is poured over silver chloride on a filter-paper, the extract will give a distinct turbidity on acidification with nitric acid. Silver bromide similarly treated gives no turbidity.

By allowing the silver salts to remain in contact with the reagent for a few minutes with occasional agitation, the chloride will give a greater turbidity on acidification, while the treatment of the bromide may be continued sometimes even for half-an-hour before it begins to give a positive result.

If a turbidity is obtained on acidification of the extract, and it is doubtful whether it is due to silver chloride or bromide, its identity may be established in the following way:—The turbid liquid is divided into two parts; to one is added a slight excess of the bicarbonate solution and to the other an equal quantity of water. If the turbidity is due to silver chloride, the ammonium salt will re-dissolve it in a few seconds. If it is due to the bromide, it will remain unaffected for several minutes, if not an hour or more. The part diluted with water is for comparison with the other, as it is difficult to bear in mind the appearance of a turbid liquid, and to duly allow for its dilution.

It is desirable that the ammonium bicarbonate solution be not old, or it will probably have lost some carbonic acid. A boiling solution of sesquicarbonate of ammonia has been used before for dissolving out silver chloride from the bromide, but in this case some of the bromide is always dissolved.

Royal College of Science, London.

THE ESTIMATION OF ORGANIC MATTER IN WATER. DISADVANTAGES OF FILTERING THROUGH PAPER BEFORE THE ANALYSIS.

By C. LENORMAND.

In a paper which I have recently published (*Bull. Soc. Chim.*, [3], xxix., 810; *CHEMICAL NEWS*, lxxxix., 219), I described a new method for the estimation of the organic matter in both fresh and salt waters.

I wish now to complete the matter, and to draw particular attention to the very considerable errors which are introduced when the waters are filtered through paper before analysis.

I have made these observations during the course of a large number of analyses of sea-water from oyster-beds. I was struck, in fact, with the very great differences obtained in the estimation of the organic matter in cases where the water was or was not filtered.

I have also tried to find whether similar differences were to be found in the case of fresh waters; and I observed that they did exist, and that they were of the same order.

Sea-water, as I have made quite sure by using the method I have described, contains a variable quantity of organic matter, but this is never so considerable as has been generally imagined, except in special cases. For example, at 4 kilometres from Cape Frehel, the amount present requires 0.900 m.grm. of oxygen per litre to destroy it; at the mouth of the Rance it requires 1.075

m.grms.; in the harbour of Saint-Malo, 1'250 m.grms.; in the Bay of Cancale, 1'433 m.grms.; in the Gulf of Gascogne, at about 200 kilometres from the shore, 1'450 m.grms. But we no longer find these or similar figures if, as a matter of precaution, we remove the suspended solid matter by means of a filter.

The remark I have just made with regard to sea-water is equally applicable to fresh waters, and further on I shall show what unexpected results are obtained with both salt and fresh waters which have been filtered before analysis.

Experiment I.

A Laurent filter of half-a-litre capacity was filled with sea-water, and the latter collected in four flasks of 100 c.c. each. The amounts of organic matter passed from 0'9 m.grm. per litre to 9'725 m.grms. for the first 100 c.c. collected, to 4'925 m.grms. for the second, 2'075 m.grms. for the third, and 1'450 m.grms. for the last.

Experiment II.

Filters of different makes were filled with water, exactly 100 c.c. of water passed through each, and the organic matter estimated by the same method.

Sea-water.—Results obtained with a Water containing 1'150 m.grms. of Organic Matter per Litre.

Nature of the filter-paper.	Diameter.		Ash.		Organic matter.	Original organic matter.
	C.m.	M.grms.	M.grms.	M.grms.		
Dreverhoff, No. 400 ..	15	0'2	2'200		1'150	
Schleicher, hard ..	9	0'77	3'450		1'150	
Dreverhoff, No. 311 ..	15	5'0	3'675		1'150	
Berzelius, No. 2 ..	15	3'7	4'400		1'150	
Dreverhoff, No. 331 ..	15	—	5'200		1'150	
Dreverhoff, No. 481 ..	15	8'0	6'000		1'150	
Laurent	15	—	7'550		1'150	

Fresh Water.—Results obtained with a Water containing 1'7 m.grms. of Organic Matter per Litre.

Nature of the filter-paper.	Diameter.		Ash.		Organic matter.	Original organic matter.
	C.m.	M.grms.	M.grms.	M.grms.		
Schleicher, hard ..	9	0'77	2'700		1'700	
Dreverhoff, No. 400 ..	15	0'2	2'725		1'700	
Berzelius, No. 2 ..	15	3'7	3'925		1'700	
Dreverhoff, No. 481 ..	15	8'0	5'325		1'700	
Dreverhoff, No. 331 ..	15	—	7'250		1'700	
Laurent	15	—	7'800		1'700	

Experiment III.

A Laurent filter of 15 c.m. diameter was filled with some of the same fresh water, containing 1'8 m.grms. of organic matter, ten separate times. 100 c.c. was put on one side after each filtration and estimated as before.

Organic Matter obtained after the successive Filtrations.

First ..	5'350	Sixth ..	2'225
Second ..	3'125	Seventh ..	2'050
Third ..	2'975	Eighth ..	1'875
Fourth ..	2'625	Ninth ..	1'800
Fifth ..	2'450	Tenth ..	1'800

What can we conclude from these unexpected results? The following:—1. That organic matter is taken up by the passing of fresh or salt water through filters, whatever may be the kind of filter used. 2. That a filter-paper, after successive washings with the same water, loses less and less organic matter, but that it is necessary to wash it a large number of times to obtain constant and exact results.

We may draw the following practical conclusions from these results:—A fresh or salt water should never be filtered before analysis, but it must be left to settle completely (even for forty-eight hours), and a sufficient quantity to make the estimation removed with a pipette. Thus we shall not be liable to such errors as I have just pointed

out, and which might be of enormous importance in deciding on the potability or otherwise of a water, or on the possible contamination of sea-water at or near oyster-beds.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 3.

TECHNICAL RESEARCH AND THE COLLEGE SYSTEM.

By W. P. DREAPER, F.I.C.

IN criticising the work of the technical colleges, many who are closely connected with their inner workings are, in spite of the familiarity which this involves, unable to answer the question so often propounded, How is it that they turn out so little original work? Assuming that these colleges are well organised, that their teaching staff is the best obtainable, that their fittings are perfect in their way, and that the stream of students through their lecture-halls is a continuous one, what is the result as measured by the original experimental work carried on in their laboratories? The professors in many of the colleges having a chemical department have answered this question recently ("Duty-free Alcohol," by T. Tyer, *Journ. Soc. Chem. Ind.*, March, 1904). In answer to the query, "Would duty-free alcohol help research in your laboratory?" they have replied, "Yes, it would help research, but no industrial research is done." Probably realising the seriousness of this statement, one professor complained that the manufacturers did not bring up subject matter for such research, and another said that all research ultimately influenced industry in the long run.

The professors, if they knew more about the position of the manufacturers, would realise that they are leaning on a broken reed when they expect help from that quarter. The average manufacturer is, for the most part, incapable of indicating lines of research to the professor. His knowledge is of a business character, and it is not likely that he will be willing to see any experimental work connected with his factory routine more or less publicly carried on in the college laboratories, possibly under the eyes of the sons of his competitors. The alternative, viz., that the work shall be conducted in the professor's private laboratory does not meet the case. For here the professor is carrying on private work for his own convenience and profit. This, if carried out on any large scale, must seriously interfere with the success of the general college work.

The effect of this has been found so injurious that the authorities have even had to interfere on behalf of the students. The days when the professor was content to occupy a chair, give two lectures a week to the senior students, and spend the rest of his time in private research have happily gone, and can never return.

The only work the manufacturers could bring before the professors lies within the function of the works experimentalist, and is already part of the every-day routine.

The result of the present state of affairs is that the research conducted in the majority of technical laboratories runs on very narrow and circumscribed lines. The chemical department, for instance, will probably confine itself to so-called "organic" research, and this, now the famous diazo reaction has been worked to death, is apparently becoming increasingly difficult to initiate. With few exceptions this fairly represents the present-day state of affairs. This is generally acknowledged to be most unsatisfactory.

Many causes are put forward to explain this state of affairs; one is that the professors and demonstrators in the technical colleges are not men who have had the general and necessary technical experience to enable them to initiate such work. They lack the habit of picking up such lines of thought as comes from the constant and close contact with industrial operations on the large scale. Lacking this power of initiation they turn on the poor

manufacturer, who, trying his best to make 5 per cent on his capital, has little time to find answer to the question put to him. As you do not supply us with ideas for research what can you expect to find of advantage to the industrial world in our laboratories? Judging by the character and volume of the published research work carried on in these institutions, and from practical experience also, the position of the senior student is equally unsatisfactory. (This remark seems to apply still more to the United States). One or two of these may be engaged on research with the professor, but except in very rare cases the student himself will be unable to start any original work from want of experience. He will miss this important and necessary part of his training.

It is assumed that students in their last year of study cannot be better employed than in research connected more or less closely with their future career. In the case where students have not a specified line of future work cut out for them such research may give the necessary impetus in a specific direction.

The position of the technical man after leaving college and entering the industrial world is a definite one. He will experiment on a real and practical scale. He will find himself surrounded by a series of operations very varied in their way, and working on a large scale, and with practical objects seldom thought of in the college laboratory.

It is at this stage that the student's practical knowledge commences; although of course his college training is necessary ground-work for his subsequent operations. This I think is hardly realised by the professors on account of the inferior position which the technical branch is supposed to take when compared with the theoretical. In his daily round the technical man will see many operations working by rule-of-thumb. This means that the trained man has not yet stepped in to offer an explanation of their working. Many ideas will probably strike him, of a more or less theoretical nature, which will be quite outside his sphere of work as a practical man. It is taken for granted that he will be unable from force of circumstances to follow up these ideas connected with the theoretical side of his work. Beyond making a mental note of them, he must pass on to the pressing demands of the day. The opportunity is not his; the work must remain undone.

We have therefore, on the one hand, students starving for want of original work, and on the other, practical men unable to conduct such work rather from want of opportunity than ideas, and far above them all the professor sitting in his chair and railing at the manufacturer for not supplying him with ideas.

All this is the outcome of the position taken up by the professor. He has looked in the wrong direction for help.

The following scheme is put forward with the idea of overcoming this more or less serious state of affairs, and bringing the student more in touch with the problems he will have to face in his future life's work. These semi theoretical, or even purely theoretical, problems arising out of the actual and practical experience of the experimentalist, are surely the very thing that "last year" students should be working on; under the present conditions this is impossible. It is not at all probable that these problems will be attacked by the technical man for want of opportunity. In this way many ideas lie dormant and unproductive.

The position of the teacher, student, and worker is therefore as follows:—The professor, from his want of practical knowledge, or want of an every-day experience in the practical matters of his profession, can only be expected to initiate research work of a purely theoretical nature, and this in doses as judged by the publication of such work. No man can, nor should be expected to, supply a department with ideas for research. A one source supply would also be one-sided in its nature. On the other hand, the professor from his position, past training, which we will assume to be of a high order, and from the time he is able to devote to general study, should be just the man to value in their early stages the ideas presented as subject-matter for re-

search. The professor is therefore made the corner stone of the scheme, which would work as follows:—

- (a). A research board would be founded in every technical or scientific college of repute, consisting of the professors and demonstrators.
- (b). Technical men who have passed through the college course (or others under certain conditions) would be invited by the Board to submit any ideas of a theoretical or semi theoretical nature which they think fit subject for research, suggested to them by their work, but owing to circumstances they are unable to carry out themselves.
- (c). The Board, after favourable consideration, would put a senior student in communication, through the Board, with the said technical man. The student, or even students, under such direction would commence a research on this special subject, carrying out the experimental part under the direction of the college staff under certain specified and general rules.
- (d). The results, if of a satisfactory nature, would be published under the name of the experimentalist. Special mention being made of the student and the college.
- (e). For the benefit of the general students research meetings would be held in class under the professor, where the aims and progress of the research would be indicated but not necessarily discussed.

In some such way as this the technical man would find a partner only too willing to engage in this kind of work. The staff control would guarantee the quality of the work done, and the Research Board would supply the connecting link between the student and the technical expert. The college should be in reality as in name a technical institution.

It might be urged that the relations of the manufacturer to the experimentalist would stand in the way of any such scheme. The experience I have collected goes to prove that this is not the case so long as the work is essentially theoretical in its nature or not too closely connected with the factory work.

For any such scheme to succeed it would be necessary that a general scheme for all colleges should be decided on, and that within certain limits outside experimentalists should be able to submit ideas to the college Board. This work, in addition to that already initiated by the staff, should afford in time sufficient material for an extended system of research, far-reaching in its scope, and also I think in its influence. It would tend to relieve the staff from the strain that it apparently is under in providing sufficient material for this purpose. It would bring the quantity of work done in this country into better comparison with that done in the European States without at the same time becoming trivial in its nature.

Lecture Experiments for the Demonstration of Mass Action.—A. v. Dieterich and Lothar Wohler.—These experiments, which serve to illustrate mass action, are based upon the influence exercised by the influence of caustic potash on calomel:—1. With a solution of KOH at 1/100th the red colouration of phthalein disappears on agitation with calomel. 2. With a solution of KOH of a strength greater than 1/100th, we do not observe the decoloration of phthalein on agitation with Hg₂Cl₂. 3. With KOH at 1/100th, in the presence of chloride of potassium, we observe an analogous phenomenon. 4. If to a solution of potash, which has been decolourised by calomel, we add a few drops of a solution of KCl, the red colour reappears. 5. Equal parts of a solution of KOH at 1/100th and saturated KCl do not react on calomel. 6. If the red solutions obtained in experiments 2, 3, and 4 are heated, the colour disappears, and reappears on cooling.—*Zeit. Anorg. Chem.*, vol. xxxiv., p. 194.

THE DECOMPOSITION OF THE FINAL FRACTIONS OF MONAZITE INTO COMPONENTS, AND THE PREPARATION OF PURE GADOLINIUM OXIDE.*

By R. MARC.

Preparation of Gadolinium Oxide.

GADOLINIUM was discovered in samarskite by Marignac in the year 1880, and was called *Ya*. He separated it from the mixture of earths by purifying the nitrates, and separated it from the samarium which he called *Y3* by fractionating with potassium sulphate. He characterised the oxide as having the highest atomic weight of those earths which resemble it in their behaviour towards potassium sulphate. Marignac's experiments were repeated by Lecoq de Boisbaudran, the existence of *Ya* was established, and with Marignac's approval the name gadolinium was given to it. Crookes examined for cathode luminescence a gadolinium prepared by himself, and established a spectrum with three lines, one in the red and two in the orange. He concluded, from the spectroscopic behaviour, that gadolinium could be split up into three components. Bettendorf, by the use of the potassium sulphate method as modified by him, prepared pure gadolinium, and proved the elementary nature and purity by the constancy of the weights and the unaltered solubility of the separate fractions in saturated potassium sulphate solution. Benedicks recently obtained pure gadolinium oxide by crystallising the nitrates, and prepared a large number of its salts. He shares the opinion which Lecoq advocates, in opposition to Crookes, that the cathode luminescence of the gadolinium is caused solely by impurities.

For the preparation of the gadolinium oxide a material was placed at my disposal by Prof. W. Muthmann; it had been prepared by Herr L. Weiss from the final chromic acid fractionations of many kilogrammes of monazite. The last fractions were again treated with chromic acid, and then the final fractions again taken. This process was repeated some few times. The last fractions formed my material. It was of a decided yellow colour, and showed in the absorption spectrum the bands of the erbium components, samarium and neodymium, but no lines of praseodymium, even with the broadest layer. This material was treated as follows (cf. the tabular statement of the progress of the fractionation, Table I.).

After careful purification I possessed only 87 grms. altogether. It is clear that to separate the single components from such a small mass extraordinarily careful work was necessary. I was soon convinced that by the ordinary method of fractionation the material would in a short time be split into nothing but small portions before it was possible to bring about a definite separation.

Before, however, I pass to the details of the work, I will mention the methods of separation which I employed. These were the ammonia, the oxalic acid, and the potassium sulphate methods.

The Ammonia Method.

The fractionation with ammonia was performed as follows:—The whole of the material was divided into portions of 30 grms. Each such portion was dissolved in hydrochloric acid, diluted with two litres of water and accurately neutralised, and very dilute ammonia solution was dropped in from a separating funnel, while the liquid was kept in continual motion by means of a glass stirrer. The quantity of the ammonia was measured so that it corresponded to about half the quantity of oxide. The corresponding fractions of the separate portions of 30 grms. were again mixed and divided by means of ammonia into two parts, &c. By this method the erbium accumulated in the precipitates and the yttria in the liquids.

The Oxalic Acid Method.

Crookes employed oxalic acid for separating terbium (*Phil. Trans.*, cxxxiv., 911). He dropped oxalic acid into the strongly acidulated boiling solution of the nitrates of the earths until a turbidity resulted, and then removed this turbidity by the addition of boiling nitric acid, and allowed to cool slowly. The oxalates then crystallise out in large crystals, which frequently enclose some mother liquor, and thus the separation is naturally delayed. To obviate this I proceeded as follows:—

The 10 per cent strongly acid solution of the nitrates was heated to boiling in a little flask, and rapidly boiling oxalic acid added until a permanent precipitate or turbidity began to form. Then the flask was cooled quickly, being vigorously agitated all the time, and the oxalates separated out as an exceedingly fine crystalline powder. The filtrate from the oxalates was concentrated to the original volume and again treated as described above.

The crystals which I obtained by this method were very small, and the results better than those obtained by Crookes's method, which I also employed for some experiments.

The Potassium Sulphate Method.

The potassium sulphate method served principally to separate didymium and samarium from the remaining earths. It was first used by Mosander. Afterwards Marignac (*Comptes Rendus*, xc., 899) investigated the solubility ratios of the double potassium sulphate salts in saturated solution of potassium sulphate.

Lecoq de Boisbaudran (*Comptes Rendus*, cii., 398) and Bettendorf (*Ann. d. Chem. u. Pharm.*, ccxvi., 160) also used this method of separation, the latter in a somewhat modified form. I generally kept to Bettendorf's directions. But first of all I distinguished two methods, according to the aim I had in view:—

1. If I wanted to separate quickly a greater quantity of material into two parts, one of which would contain the greater part of the colourless earths and the other the greater part of the neodymium and samarium, then the following method was adopted:—

The neutral, or only very slightly acid, concentrated solution of the nitrates was introduced into a 4-litre flask, which was filled with a concentrated solution of potassium sulphate, the bottom being covered with crystals of this salt. The flask was filled up to the top with potassium sulphate solution, closed and sealed, and turned upside-down. This was done to prevent the settling of the precipitate formed on the bottom of the flask. The separation of the double salt begins at once. As soon as the liquid has cleared, which takes 1 to 2 hours, it is drawn off. With 4 litres of liquid about 10 grms. of the earths go into solution.

The precipitate was treated as is further described below, converted into nitrate, and then another 10 grms. brought into solution by the same method. This process was repeated as long as the oxide which went into solution showed no absorption streaks of neodymium and samarium, or only showed them very faintly. Thus the material had been divided into two parts, the first of which consisted of all the earths which had gone into solution, and the second of the part which had remained undissolved.

II. But when it was a question of obtaining from a material which contained neodymium and samarium the colourless earths, quite free from these two substances, disregarding the smallness of the results and the waste of time, the following method was used:—

According to the quantity of the material a 1 to 2 litre flask was only half filled with a concentrated solution of potassium sulphate. The bottom was covered with crystals, the concentrated neutral solution of the nitrates introduced into it, the flask closed and shaken on a shaking machine, with short interruptions, for two to three days. Almost the whole of the earth goes into the precipitate, and only 1 to $\frac{1}{2}$ grm. remains in solution. The solution was, however, always quite free from neodymium and samarium,

* From the *Zeitschrift für Anorg. Chemie*, xxviii., 121.

even if they were contained in the original material in considerable quantity. If the material contained no colourless earths, generally nothing, or only minute traces, went into solution. The treatment could be repeated until all the earths of the yttrium group were removed; but these operations, even with small quantities of material, would take months.

Concerning the treatment of the solutions and precipitates obtained, the following remarks must be made:—The solutions were simply treated with ammonia, the hydroxides precipitated were filtered off, dissolved, precipitated with oxalic acid, and the oxalates ignited. The precipitates of double sulphate could not be dissolved in water. Bettendorf (*loc. cit.*) treated them with hydrochloric acid, but it is necessary to use a very large quantity of acid and to heat for hours in order to bring them entirely into solution. For this reason I decomposed the double sulphates with sodium carbonate.

About an equal quantity of sodium carbonate and a little water were added to the double salts, and the mixture was heated to boiling for some time. By this means the double sulphate is completely converted into a basic carbonate, which again, for the most part, dissolves in the excess of sodium carbonate. Hydrochloric acid is then added until carbonic acid is no longer evolved; the earths are first precipitated as carbonates, and then dissolve in the excess of hydrochloric acid. If a residue remains still undissolved, this is again heated with soda, otherwise the earths are precipitated immediately from the hydrochloric acid solution by means of ammonia, and are filtered off, dissolved, precipitated with oxalic acid, and the oxalates ignited.

The whole quantity of the material at my disposal was treated with potassium sulphate by method I., in order to separate it into two groups, the one containing the yttria, erbium, terbium, and gadolinium, and the other the neodymium and samarium. Altogether four fractionations were necessary for this purpose. The four solutions together formed the first group and amounted to 45 grms.; the undissolved residue formed the second group and amounted to 42 grms.

The oxides of group I. showed only very faintly the bands of neodymium and samarium. They were decomposed into two parts by a series of ammonia fractionations, and of these two parts one did not show the slightest trace of the erbium spectrum, and the other no trace of neodymium or samarium. To avoid a loss of material I fractionated by the following method:—

The oxides were divided by means of ammonia into two equal parts, a precipitate and a filtrate, and precipitate and filtrate were each divided into two halves. In this way a series of four members was obtained. The two middle members were then further treated, and those parts which corresponded to the first or fourth members, as regards their spectra, were added to these members respectively. Thus the whole of the material was divided into two halves, separated by four fractionations. Each of these two halves was again divided. The extreme members were already separated by six fractionations, and the middle members were again treated till they were all added to the two extremes. Thus it was possible, by a series of 36 fractionations, to divide the material into two totally different parts without the least loss. The great number of fractionations necessary for such a separation is easily understood when we consider that the number of operations necessary to bring the inner members to the same state of purity as the outer is always greater the further the outer members are separated from one another.

The first thing to do was to find out in which part of the above mentioned separation the gadolinium would first be.

As the gadolinium is more strongly basic than erbium, it was to be assumed that it would be contained in the second part of the separation, which was shown by its spectrum to be free from erbium, and was far less yellow. This part was therefore again fractionated with ammonia.

according to the above scheme. Altogether about forty operations were performed, but in the last series of fractionations the separate members were not combined in two, but in three groups, according to the magnitude of their atomic weights. (In order to avoid converting from equivalent weights to atomic weights in dealing with mixtures, I have retained the expression atomic weight and calculated to the formula R_2O_3).

The oxides with atomic weight 125–139 are in the first group. They were so largely adulterated with yttrium earths that it was worth while treating for gadolinium. There were altogether 10 grms. of yellow coloured oxides, which were almost free from absorption bands. The fractions 140–147 occurred in the middle group, amounting altogether to 10 grms. These oxides possessed a fainter yellow colour, and showed the samarium lines clearly and the neodymium lines faintly. The third portion showed the neodymium bands very strongly, and in addition, the samarium bands faintly. There were altogether 5 grms. of oxides of the greyish blue colour which is peculiar to neodymium oxide.

The high atomic weight of the second group leads us to infer the presence of a high percentage of gadolinium, as it could not, in any case, be caused by the comparatively small quantity of samarium. The gadolinium was thus adulterated in this group, on the one hand by yttria, and on the other by samarium and neodymium in small quantities. It was evident that it could not be easy to isolate in a pure condition one component from 10 grms. of such a mixture. Marignac's (*Comptes Rendus*, xc., 899) statements that yttria was soluble in less than 100 parts of potassium sulphate, gadolinium in about 200 parts, while samarium was only soluble in 400 parts, and neodymium was practically insoluble, led me to perform the separation with potassium sulphate, according to the method given under II.

The concentrated neutral solution of the nitrates was each time shaken vigorously for three days with 500 c.c. of concentrated solution of potassium sulphate, when the following amounts went into solution successively:—

I. 0.46 gm. oxide	Atomic weight, for R_2O_3	117.8
II. 0.474 "	"	121.15
III. 0.624 "	"	142.7
IV. 0.472 "	"	150.8
V. 0.45 "	"	153.7
VI. 0.41 "	"	151.78

(Free from neodymium and samarium).

The above numbers show that the solubility of the gadolinium in a saturated solution of potassium sulphate is considerably less (about one-tenth) than that stated by Marignac (*loc. cit.*). The reason for this is that on standing at rest strongly supersaturated solutions are formed. I hope to be able to communicate more accurate investigations of this point soon.

All the oxides of this series were quite free from absorption spectra. The first members were decidedly yellow, the last only faintly. The last member with atomic weight 154.78, resembled gadolinium most closely, the following figures being given by the various authors as its atomic weight:—Marignac, 156.75; Lecoq de Boisbaudran, 155.9; Cleve, 155; Bettendorf, 156.33; Benedicks, 156.38. My preparation was doubtless still adulterated with small quantities of yttria.

The residue (7 grms.), which did not go into solution with potassium sulphate solution, was again subjected to treatment with the same solvent. But it was not possible to bring more substance free from samarium into solution. However, I succeeded in completely removing the small quantities of neodymium by once applying potassium sulphate method I., and was also successful in removing the greater part of the samarium. From the material (3 grms.) thus obtained, which contained a small amount of samarium, I was able, by a long series of exceedingly carefully performed ammonia separations, to obtain $\frac{1}{2}$ gm. of

oxide free from samarium, and determine its atomic weight. The determinations gave:—

I. 0.2201 grm. of oxide gave
0.3666 grm. of sulphate.

Difference 0.1465 grm.; hence atomic weight = 156.3.

II. 0.2444 grm. of oxide gave
0.4070 grm. of sulphate.

Difference 0.1626 grm.; hence atomic weight = 156.35.

These two numbers agree satisfactorily with the values 156.33 and 156.38, given by Bettendorf and Benedicks.

After strong ignition gadolinium oxide is only faintly yellow. It is difficult to say definitely whether this suggestion of a yellow colour is characteristic of gadolinium oxide or is due to the admixture of traces of a coloured earth. But it is a fact that a specimen of gadolinium which does not show this colouration has not yet been obtained. The colour disappears in a current of hydrogen.

The salts, and the solutions of the salts of gadolinium, are colourless. The solutions show no absorption spectrum. Under the influence of the cathode rays neither pure gadolinium sulphate nor oxide becomes luminescent, and no cathode luminescence spectrum is shown. (Cf. Baur and Marc, *Ber. Deutsch. Chem. Ges.*, xxiv, 2460-66).

There can hardly be any further doubt concerning the elementary nature of gadolinium. If gadolinium were a mixture, neighbouring earths with atomic weight higher than 156 would be known to us. However, this is not the case, the atomic weight 156 of gadolinium being, as Marignac has already noticed, the highest of the earths standing near it.

The atomic weight determinations were performed by Krüss's method (*Zeit. Anorg. Chem.*, iii., 44-59), by the conversion of the oxides into sulphate. Previous to the determination the oxides were carefully purified.

The chief impurities were platinum, iron, calcium, aluminium. The oxides were therefore dissolved in acid. The excess of the latter was neutralised with ammonia, and sulphuretted hydrogen was passed in for 6 hours. After filtering and concentrating the solution, it was precipitated with ammonia in presence of ammonium chloride, filtered, washed, dissolved, again precipitated with ammonia, thoroughly washed, again dissolved and finally precipitated from a slightly acid solution with the purest oxalic acid, the oxalate being thoroughly washed and ignited. These operations were not always sufficient to remove the last traces of iron. Hence, if the solution of the oxides still gave iron reactions, the hydrochloric acid solution was concentrated until it began to crystallise. The iron remained in solution when all the earths had crystallised out.

0.2 to 0.4 grm. of the purified oxides were then heated in a porcelain crucible until the weight became constant, in order to ensure the absence of carbonic acid and moisture. These oxides were then very carefully moistened with two or three drops of water, and enough dilute hydrochloric acid was added to dissolve them. Then they were heated over a small flame on an iron plate about 5 m.m. thick until they were completely dissolved. 1 to 2 c.c. of dilute sulphuric acid were then added carefully by means of a small pipette, and the liquor evaporated on the iron plate over a very small flame till the sulphate began to crystallise. When crystallisation began the flame was raised. When no more acid fumes came off the flame was brought close up under the iron plate. After some time the crucible was placed on a pipeclay triangle and heated over an open flame, which was at first small, but was afterwards gradually raised, without, however, being allowed to approach within 2 or 3 c.m. of the bottom of the crucible. Heating for 4 to 6 hours was generally sufficient, and a second weighing was almost always constant.

Samarium.

For the preparation of samarium I had the choice of the neodymium preparations, rich in samarium, or the middle

preparations, less rich in samarium but quite free from neodymium. I decided to use the latter, as it is far more difficult to separate samarium from neodymium than from erbium, and it was important for me to get a preparation quite free from neodymium.

The material for the preparation of the samarium consisted of only 10 grms. of atomic weight 125 to 139. It possessed a well-marked yellow colour; its spectrum showed, besides decided quantities of samarium, small quantities of erbium, but no neodymium. The separation of the samarium from the erbium is performed comparatively easily.

Ammonia was used for the separation, and I arranged so that only as much ammonia was added as corresponded to 1 grm. of the oxide. Even after the first three fractionations the remaining liquid appeared quite free from erbium. To make quite sure two more fractionations were performed, and the remaining 5 grms., which were quite free from erbium, were treated in such a manner that those oxides which showed the samarium spectrum most strongly were united, purified, and further fractionated. After rather a long series of fractionations I finally obtained, as the richest in samarium, 0.2 grm. of a yellow preparation, which was quite free from absorption bands of foreign earths.

It was interesting to observe whether this samarium oxide, when mixed with lime or yttria like the three other earths with absorption bands, would give a cathode luminescence spectrum. This was, however, not the case.

The cathode spectrum characteristic of neodymium and erbium was indeed faintly visible, and, as in the case of yttria, it may safely be stated that a complete elimination of this spectrum is hardly possible, owing to the sensitiveness of the method.

The absorption spectrum of my samarium preparation showed the two following bands:—

λ 487-475 and λ 467-462,

while Lecoq de Boisbaudran gives as the middle of the samarium bands (*Berichte Deutsch. Chem. Ges.*, xxv., 2382):—

λ 480 λ 463 λ 417 λ 400.75.

I could not see either of the two last.

From the material on the right-hand side by repeated fractionation with ammonia I could also get preparations very rich in samarium, but these retained the last traces of neodymium with extraordinary energy.

I also succeeded in preparing from the extreme fractions 9 grms. of almost perfectly pure neodymium, which were adulterated with only very small quantities of samarium.

The left-hand side is very interesting. By alternate fractionations with ammonia and oxalic acid, first erbium and then holmium (λ 454-449) could be separated, and finally the brown ochre terbium preparations were obtained with the bands λ 464-461, which are probably characteristic of terbium, and of which I gave an account some time ago (*Ber. Deutsch. Chem. Ges.*, xxv., 2382).

This work is an unpublished part of a more extensive piece of work which I have been doing for two years in Prof. W. Muthmann's laboratory in the Technical High School at Munich. Its chief aim is to examine the usefulness and application of methods of separation of the rare earths, methods which made it possible to separate from a relatively very small quantity of material single components in a pure state (neodymium, samarium, gadolinium), and to increase the proportion of others so that it was possible to make observations of their properties (terbium).

Application of Blondlot Rays to Chemistry.—Albert Colson.—The author's experiments show that the Blondlot rays are probably due to the formation of basic salts. This kind of molecular condensation produces analogous effects to those which are obtained by mechanical compression.—*Comptes Rendus*, cxxviii., No. 15.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, April 20th, 1904.

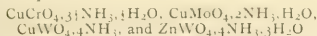
Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

(Concluded from p. 224).

65. "Ammoniacal Double Chromates and Molybdates." By SAMUEL HENRY CLIFFORD BRIGGS.

A number of double salts of ammonium chromate belonging to a series of compounds having the general formula $M_2M^{II}(RO_4)_2 \cdot 2NH_3$ have already been described (*Trans.*, 1903, lxxxiii., 391). Other members of the same series have now been prepared, M^I being either NH_4 or K ; M^{II} being Cu , Zn , Cd , Co , or Ni , and R indicating either Cr or Mo . The corresponding tungstates could not be obtained.

The compounds—



have been incidentally prepared during the investigation.

66. "The Hexahydrated Double Chromates. Magnesium and Nickel Compounds." By SAMUEL HENRY CLIFFORD BRIGGS.

The double chromates $M_2M^{II}(CrO_4)_2 \cdot 6H_2O$, in which M^{II} is magnesium or nickel and M^I is K , Rb , or Cs , have been prepared.

The nickel compounds were obtained by adding a solution of the alkali chromate to a solution of nickel acetate, at the ordinary temperature for the rubidium and caesium salts, and at 6° for the potassium compound.

The magnesium compounds crystallised out when cold concentrated solutions of their components were mixed, the preparation of the potassium salt being carried out at -10° .

Both the potassium compounds are very efflorescent at the ordinary temperature, whilst in the case of the series of salts in which M^{II} is the same, the stability increases with the atomic weight of the alkali metal. This variation is in the same sense as that found by Tutton (*Trans.*, 1896, lxxx., 521) for the relative stabilities of the corresponding double sulphates.

67. "Hydrocellulose." By CHARLES FREDERICK CROSS and EDWARD JOHN BEVAN.

The residues described by Stern (*Trans.*, 1904, lxxxv., 336) having the empirical composition of cellulose are no doubt products of hydrolysis and reversion, and are constitutionally different from the original cellulose; but they are in no case identical with those described by Girard, and therefore this investigator's exhaustive account of the actions of acids on cellulose remains unaffected by the criticisms contained in the above-mentioned paper. The statements (*loc. cit.*) as to the causes of the attendant structural changes are, moreover, improbable.

Cellulose is a chemically labile and structurally plastic aggregate, occupying an intermediate position between the two extremes, determined by the action of (a) alkali hydroxides, (b) the halogen hydrides, both in presence of water.

It is suggested that the terms hydracellulose and hydro-cellulose respectively may for the present be retained to designate the two groups of derivatives obtained by the processes (a) and (b).

68. "Borylcarbimide." By MARTIN ONSLOW FORSTER and HERBERT MOORE ATTWELL.

The appearance of a paper by Dohrt and Haager (*Monatsh.*, 1903, xxiv., 844), dealing with the production of phenylcarbimide by the action of nitrous acid on phenylcarbamide, leads us to record a similar observation which we have made in connection with borylcarbamide.

Borylcarbimide, $C_{10}H_{17}N \cdot C \cdot O$, prepared by adding solid sodium nitrite to borylcarbamide nitrate suspended

in water at 0° , is a colourless, crystalline substance which melts at 72° ; it is very volatile, and the vapour is intensely pungent. A 2 per cent solution in benzene has $[a]_D + 46.5^\circ$. It is hydrolysed by acids and alkalis, yielding borylamine, whilst aniline converts it into borylphenylcarbimide, previously obtained from borylamine and phenylcarbimide (*Trans.*, 1898, lxxiii., 393).

Diborylthiocarbamide, $S \cdot C(NH \cdot C_{10}H_{17})_2$, obtained on heating borylamine with carbon disulphide and alcohol until hydrogen sulphide is no longer liberated, melts at 227° .

Borylamine boryl lithiocarbamide,—



is produced at the same time, and melts at 78° .

Borylamine thiocarbamide crystallises from hot water in long, lustrous needles melting at 178° ; above this temperature, it changes into diborylthiocarbamide.

69. "Reduced Silicates." By CHARLES SIMMONDS.

The substance left when lead silicates are reduced by heating in hydrogen (*Trans.*, 1903, lxxxiii., 1449) is in general shown to be a compound which can be regarded as a combination of the metal and silica, in the same sense as the original silicate is a combination of the metallic oxide and silica. In some cases, however, a certain proportion of metallic lead is mixed with the substance; this occurs when the original silicates (for example, orthosilicates and basic silicates) contain a greater number of basic than of acidic oxides in the silicate molecule.

The reduced residues are generally more refractory than the original silicates. Treatment with the commoner acids and oxidising agents has little effect on them, but they are decomposed by hydrofluoric acid and by fusion with alkali carbonates. The term "silicites" is suggested for these reduced silicates.

Similar results were obtained with the silicates of copper, iron, nickel, and cobalt.

70. "Picryl Derivatives of Urethane and Thiourethane." By JAMES CODRINGTON CROCKER and FRANK HAROLD LOWE.

The authors show that the reaction between picryl chloride, thiocyanates, and alcohols is due to the formation of the ψ -thiourethanes, $PiN \cdot C(SH) \cdot OX$, as intermediate products, which subsequently react with picryl chloride, and pass into the picriminothiocarbonates, $PiN \cdot C(SPi) \cdot OX$. The results obtained with the cyanates, picryl chloride, and alcohol confirm this view. Under these conditions, the corresponding urethanes, $PiNH \cdot CO \cdot OX$, are formed, and in the case of ethyl alcohol, the picriminocarbonate, $PiN \cdot (OEt) \cdot OPI$, is also produced. The following compounds are described:—

Picryl isopropyl picriminothiocarbonate, melting at 147° , and the corresponding amyl ester (m. p. 138.5°), picryl-methylurethane (192°), picryl-ethylurethane (147°), picryl-n-propylurethane (139°), picryl-isopropylurethane (177.5°), picryl-isobutylurethane (134°), picrylamylurethane (131°), picryl ethyl picriminocarbonate (222°). Picryl thiocyanate is a crystalline powder which does not melt, but decomposes on heating.

The urethanes are tautomeric, the solutions in associated solvents being coloured, whilst those in non-associated solvents are colourless.

71. "The Oxime of Mesoxamidi (iso-Nitrosomalonomide) and some Allied Compounds. Part III. Tetra-substituted Derivatives." By MARTHA ANNIE WHITELEY.

In a previous communication (*Trans.*, 1903, lxxxiii., 43) reference was made to isonitrosomalondimethylanilide, $C_{17}H_{17}O_3N_3$ (m. p. 109°)—a tetra-substituted derivative of isonitrosomalonomide—and to a compound (m. p. 192°), described as isomeric with it, which was obtained together with the corresponding ketone (m. p. 172°) by the action of nitrosyl chloride on malondimethylanilide. Although the examination of this abnormal reaction is still incomplete, the present note is put forward in consequence of the

appearance of a paper on isonitrosomalonalanide by Ratz (*Monatsh.*, 1904, xxv., 55).

The compound melting at 192° (mol. wt. in naphthalene = 311) has the formula $C_{17}H_{11}O_3N_3$ or $C_{17}H_{11}O_3N_3$, and on reduction with zinc dust and acetic acid or with aluminium amalgam, yields a compound, $C_{17}H_{17}O_3N_3$ or $C_{17}H_{19}O_3N_3$, which crystallises in colourless, prismatic needles, and melts at $185-186^\circ$. When treated with alcoholic potassium or sodium hydroxide, it forms crystalline alkali salts, and from their solutions mineral acids precipitate a crystalline acid, $C_9H_5O_3N_2$, melting with decomposition at 256° , which yields an ethyl ether, $C_9H_5O_3N_2Et$ (mol. wt. in naphthalene = 222), crystallising in octahedral prisms, and melting at 168° .

Aminomalondimethylanilide, $(CO \cdot NPhMe)_2CH \cdot NH_2$, prepared by reducing isonitrosomalondimethylanilide with zinc dust and acetic acid, forms highly refractive prisms melting at 108° .

Nitromalondimethylanilide, $(CO \cdot NPhMe)_2CH \cdot NO_2$, obtained together with the compound melting at 192° by the action of fuming nitric acid on isonitrosomalondimethylanilide dissolved in chloroform saturated with nitrosyl chloride, forms colourless prisms melting with decomposition at 156° , yields crystalline, yellow alkali salts, and is readily reduced by zinc dust and acetic acid to mesoxdimethylanilide. When boiled with piperidine in alcoholic solution, nitromalondimethylanilide yields a white crystalline compound melting at 184° , probably *dihydroxymalondimethylanilide*, $(CO \cdot NPhMe)_2C(OH)_2$, which has also been prepared from isonitrosomalondimethylanilide by a similar method or by the action of potassium hypobromite.

Malonitraphenylamide, $(CO \cdot NPh)_2CH_2$, prepared by the action of diphenylamine on malonyl chloride, crystallises in colourless prisms melting with decomposition at $219-220^\circ$. The isonitroso-derivative, $(CO \cdot NPh)_2C:N \cdot OH$, forms pale yellow prisms melting with decomposition at $237-238^\circ$. The potassium salt, $(CO \cdot NPh)_2C:N \cdot OK$, forming slender, yellow needles, gives with ferrous sulphate the rich bluish-purple precipitate characteristic of this group of oximes, and regenerates the isonitroso-compound on treatment with mineral acids or carbon dioxide. The acetyl derivative (pale yellow prisms, m. p. 190°), the benzoyl derivative (colourless prisms, m. p. 175°), and the ethyl ether (m. p. $164-165^\circ$) have been prepared. The amino-derivative, $(CO \cdot NPh)_2CH \cdot NH_2$, crystallises in colourless prisms, and melts at $200-201^\circ$.

Nitromalonalanilide, $(CO \cdot NPh)_2CH \cdot NO_2$ (m. p. 141°), is obtained together with a compound melting at 128° by the action of fuming nitric acid on isonitrosomalonalanilide dissolved in chloroform saturated with nitrosyl chloride. The amino-derivative, $(CO \cdot NPh)_2CH \cdot NH_2$, forms white scales melting at $141-142^\circ$.

Malonnonophenylamide, $NHPh \cdot CO \cdot CH_2 \cdot CO \cdot NH_2$, crystallises with $\frac{1}{2}H_2O$, and, when anhydrous, melts at $153-154^\circ$ (Freund gives 163°); the isonitroso-derivative, $NHPh \cdot CO \cdot C(CO \cdot NH_2) \cdot NOH$, forms needles melting at $180-181^\circ$ with decomposition.

The investigation of the derivatives of isonitrosomalonalanide is being continued.

THE FARADAY SOCIETY.

An Ordinary Meeting was held on May 9th, 1904, at the Institution of Electrical Engineers, Mr. BERTRAM BLOUNT in the Chair.

Dr. CHARLES E. FAWCITT read a Paper entitled "*Studies in Viscosity.*"

Some Relations of Viscosity to Salt Formation.—The viscosity of a mixture of two or more substances in aqueous solution is equal to the product of the viscosities which the solutions of the substances separately have. If, however, the substances act chemically on one another then the viscosity of the mixture is different from the calculated value. By numerical illustrations from cases where a strong acid is neutralised by a strong base, this

difference is shown to have a constant value for equimolecular quantities. This value corresponds to the formation of undissociated water from the hydrogen and hydroxyl ions. The difference between the calculated and observed values, in the case where a weak base is mixed with a strong acid, has a value which varies with the base in the case of urea, and its derivative appears to vanish.

Viscosity as an Additive Property.—A comparison of the viscosity constants of some urea derivatives and aurides of the fatty series shows that, for a difference in the composition of CH_2 , there is a corresponding difference in the viscosity constant. There is, however, a pronounced "constitutional" effect, as shown by the different values obtained for isomeric substances.

Mr. B. BLOUNT referred to the difficulties in making accurate and reliable viscosity measurements on which important deductions are based.

Dr. T. M. LOWRY discussed the relationship between viscosity and conductivity, and conductivity and temperature; and he showed how, in the case of very dilute solutions, the conductivity-temperature curves converge to zero conductivity at $-39^\circ C.$, just as the viscosity curve for pure water does.

Dr. RUDORF observed that with different forms of apparatus different results are obtained.

Dr. FAWCITT, in reply, said that his results were all obtained with one apparatus, and that they were strictly comparable. Referring to Dr. Lowry's remarks, he added that viscosity is inversely proportional to migration velocity.

Dr. F. M. PERKIN then read a Paper by A. FONTANA and himself on "*The Electrolytic Oxidation of Anthracene.*"

The authors have taken up the study of the oxidation of anthracene, primarily to ascertain whether it was possible to obtain a good laboratory method for the preparation of anthraquinone. The first attempts were made with solutions in acetone, platinum electrodes being employed. Although oxidation took place in solutions of anthracene in acetone, it was not found possible to oxidise more than about 55 per cent of the anthracene. Attempts were then made to electrolyse anthracene suspended in 20 per cent sulphuric acid, or in caustic alkali, to which an oxygen carrier had been added. Various carriers were employed, the most satisfactory being chromium, cerium, or manganese salts. The anode consisted of a lead vessel; the cathodes, four in number, were also of lead and were placed in four small porous cells. There was also a lead paddle, which was connected with the positive pole. The total anode surface was about 6 square decimetres; current density, 1 ampère per square decimetre; temperature, $70-80^\circ C.$; and E.M.F. from 2.5 to 3.5 volts. The yield of anthraquinone was about 10 per cent, and it was not found possible to increase the yield more than 1 or 2 per cent above this. It was afterwards found that almost equally good results were obtained without a diaphragm. In this case the stirrer, $\frac{1}{2}$ square decimetre in area, was made the cathode. In discussing the results of their experiments, the authors consider that, owing to its volatility and the comparatively poor yield, a solution in acetone cannot be recommended. On a large scale no method in which a diaphragm is employed would be satisfactory, owing to the migration of the $SO_4^{''}$ ions from the cathode to the anode side. They then briefly review the patents of the Höchst Farben Fabrik, Darmstädter, and Martin Moest. Le Blanc criticised Darmstädter's patent and doubted whether it would be possible to obtain any appreciable quantity of anthraquinone owing to the reduction of the chromate by the cathodic hydrogen. The authors are of the opinion that to a certain extent the chromium, manganese, and cerium salts act as chromium does when employed in the electrolytic bleach industry, viz., by prevention of reduction. Moest claims, in his patent, to obtain 100 per cent yields of anthraquinone. The authors have been unable to obtain much more than 80 per cent; they are, however, of the opinion that very likely better results would be obtained on a manufacturing scale.

Mr. BLOUNT suggested the use of thallium salts. He thought the energy bill in this instance might not necessarily be an all important item.

Dr. STEINHART thought better results would be obtained if the anode solution were removed from the cathode.

Mr. INGLIS discussed the effect of the potential difference between the anode and solution.

Mr. GASTER thought the cost of energy was of prime importance. He suggested the use of petroleum as a base for colours instead of tar.

OBITUARY.

PROF. A. W. WILLIAMSON, F.R.S.

It is with great regret we record the death of Prof. A. W. Williamson, which occurred on Friday last, May 6, at his residence at Hindhead.

Prof. Williamson had only just completed his eightieth year; his health had been gradually failing for the past two or three years, but it is only about a month ago that his condition began to cause any anxiety.

With his death another of the most prominent early workers in modern chemistry is lost to us; in fact, of the six Past Presidents of the Chemical Society who had been Fellows for half a century, to whom a banquet was given on November 11, 1898, one only, Dr. William Odling, is left. The other five, Sir Joseph Gilbert, Sir Edward Frankland, Sir Frederick Abel, Dr. J. H. Gladstone, and now Prof. A. W. Williamson, have joined the great majority.

Dr. Williamson was born on May 1, 1824, and after some years of chiefly private education, he studied at the Universities of Heidelberg and Giessen, under Gmelin and Liebig. At Giessen he published his first chemical researches. He afterwards spent three years in Paris, studying the higher mathematics. In 1849, he was appointed Professor of Practical Chemistry in University College, London, and in 1855 Professor of Chemistry in the same College, still retaining the chair of Practical Chemistry. Soon after his first appointment at University College, Prof. Williamson published his researches on "Etherification and the Constitution of Salts," for which important and successful work he was awarded the Royal Medal of the Royal Society. In this research he struck at the very root of the chemical problems connected with atomic and molecular weights, and realised and cleared up those mysterious modes of explanation, such as contact or catalytic action, which before his time were always introduced when no other explanation was forthcoming; in fact, the chemistry of our time would not be the science that it is but for the work of Williamson. He was also one of the first to introduce the idea of dynamics into chemical science, and his suggestion of the dynamical theory of the voltaic battery, and of dynamic mobility in apparent stability, has been extremely fruitful in more recent years.

Among the more important papers written by Prof. Williamson we may call attention to the "Dynamics of the Galvanic Battery," in 1864; one on "The Classification of the Elements in relation to their Atomicities," and one on "Chemical Nomenclature and Notation"; all three in the same year.

In the year 1865, Prof. Williamson made an investigation which is of peculiar interest at the present time; this was on the "Composition of the Gases Evolved by the Bath Spring called the King's Bath," and he read a paper bearing this title at the Birmingham meeting of the British Association in that year. The composition of these gases was found to be over 96 per cent of nitrogen, about 3 per cent of carbonic acid, 0.5 to 0.6 per cent of oxygen, and about 0.2 per cent of marsh-gas. In conjunction with Dr. J. W. Russell, he wrote a paper on "A New Method of Gas Analysis," and in the year 1881, as President of the

Chemical Section at the York Meeting of the British Association, he delivered an Address on "The Growth of the Atomic Theory."

Prof. Williamson was elected a Fellow of the Chemical Society in 1848, and was twice President, in 1863 and 1866. He was elected Fellow of the Royal Society in 1855. In 1873 he was President of the British Association at Bradford, and was elected Treasurer in the following year. In 1875 the Royal Academy of Science at Berlin elected him a corresponding member of the Section of Physics and Mathematics, and in the same year he was appointed a member of the Senate of the University of London, in which institution he took an active part in promoting the establishment of degrees of Science. In 1887 he resigned his Professorship at University College, and was elected Emeritus Professor. He was a member of many learned societies both at home and abroad, and held the Honorary Degree of LL.D. of the Universities of Dublin and Edinburgh. In 1855 he married the third daughter of the late Prof. T. Hewitt Key, who survives him; he also leaves a son and a daughter.

NOTICES OF BOOKS.

Descriptive Chemistry. By LYMAN C. NEWELL, Ph.D. In Two Parts. London: D. C. Heath and Company. 1904. Pp. 590.

THIS book is conveniently divided into two parts, each part forming a separate volume. Part I. contains the text of the facts, laws, and theories of chemistry, and Part II. contains the experiments. The text has been selected and arranged with special reference to the requirements of teachers as well as of students, and the experiments have been prepared to meet the needs of schools in which the time available for laboratory work is short.

The book is well got up and printed, but though published in England its origin is undoubtedly American, as is shown by the quaint spelling. An excellent feature is the good index; this covers no less than 70 pages of two columns each, and is of the most comprehensive character.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 15, April 11, 1904.

Electric Osmosis in Methylic Alcohol.—A. Baudouin. —Electric osmosis is quite perceptible in methylic alcohol, but considerably less than in water under the same conditions. A difference of potential of 250 to 300 volts is necessary, as against 60 to 100 for water. The first experiments were made with absolute alcohol, but the author afterwards found that the presence of a small quantity of water did not materially affect the results.

Calculation of the Heat of Combustion of Nitrated Organic Compounds.—P. Lemoult.—In various former publications the author shows that the heat of combustion of organic compounds, $C_xH_yO_p$, can be calculated by utilising the formula—

$$Z = 102.1 + \frac{55}{2} - \Sigma fu + A.$$

The same method may be adopted for compounds which contain nitrogen, by using the new conventions,—

$$fu - a - z = \frac{1}{2} fu - a - z = \frac{1}{2} fu - (N - 1) \text{ cal.}$$

and—

$$t(a - 11) = 2 \text{ cal.}$$

These formulæ gave satisfactory results, as can be shown by the 140 cases examined.

A New Method of obtaining Calcium Carbide.—L. M. Bullier.—The author draws attention to the fact that in 1895 he described a method for preparation of calcium carbide founded on the same principles as that described by M. Moissan in a recent paper.

Estimation of Nitrogen.—Léon Débourdeaux.—The author describes a new method of estimating nitrogen, founded on the action of the alkaline monosulphides on nitrogen compounds in presence of various salts, chiefly the alkaline hyposulphites. The reaction takes place in a bulb communicating with a modified Schlœsing's apparatus. The ammonia produced is received in excess of pure hydrochloric acid, and can be estimated accurately by weighing. This method, although limited directly, can be applied to a general estimation of nitrogen after having modified the radicle containing the nitrogen by adding phenol or acid functions, or by attaching the nitrogen group to a radicle containing a phenol or acid function.

Influence of Hydriodic Acid on the Oxidation of Sulphurous Acid.—A. Berg.—Hydriodic acid, according to the quantity present, retards or accelerates the oxidation of sulphurous acid. For each solution of this latter there seems to exist a proportion of hydriodic acid which has no influence on the oxidation. For 4 per cent solutions the proportion is 3 per cent—corresponding to rather less than 1 molecule of hydriodic acid to 3 of sulphuric acid. Hydriodic acid is not the only body which accelerates the oxidation of sulphurous acid. The same is true of manganous chloride and ferrous chloride. This is a similar effect to their oxidising influence on organic substances. Soluble metallic iodides act in the same way. On the contrary, chloride and bromide of potassium have no action. Finally, hydrochloric acid retards the oxidation, and when strong may even annul it altogether.

Chloruration of Phenyl Carbonate in presence of Iodine.—Et. Barral.—The author has previously described the preparation of a neutral bichlorated phenyl carbonate, $\text{CO}(\text{OC}_6\text{H}_4\text{Cl}_2)_2$, by chloruration of phenyl carbonate in presence of iodine, and also the formation of neutral pentachlorophenyl carbonate, $\text{CO}(\text{OC}_6\text{Cl}_5)_2$, by the reaction of carbon oxychloride on pentachlorophenol. He further investigated the possibility of obtaining all the chlorine derivatives of phenyl carbonate, either by direct chloruration in presence of energetic chlorinating agents, or by synthesis by means of carbon oxychloride and the chlorophenols. By chloruration in presence of iodine, of aluminium chloride, or antimony pentachloride, and by varying the method of operation, the author now succeeds in obtaining all the degrees of chlorination of phenyl carbonate. He also establishes the fact that the chloruration of phenyl carbonate can be effected in presence of anhydrous ferric chloride.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 14.

Production of Crystallised Salts of Bismuth.—A. de Schulten.—Already inserted in full.

A Particular Property of some Hydrated Salts.—A. de Schulten.—Already inserted in full.

A Method for the Crystallisation of slightly Soluble Bodies.—A. de Schulten.—Already noticed.

The Arsenides of Copper.—Albert Granger.—Already inserted in full.

The Estimation of Vanadium in its Alloys.—Paul Nicolardot.—Already noticed.

History of the Acetals of the Polyatomic Alcohols of the Sugar Series. New Researches on the conditions of Combination of Mannite and of Paraldehyde. —J. Meunier.—Early in his research the author found that ethylic aldehyde and its product of condensation, par-

aldehyde, gave a compound with mannite as easily as benzoic aldehyde; an analogous compound was also furnished by valerianic aldehyde, but much more slowly. One of the characteristic properties of these new bodies is that of decomposing on boiling with acidulated water, regenerating the constituent aldehyde and polyatomic alcohol. The aldehyde being volatile is carried off by the steam, and thus separated from the alcohol which remains in solution. As, on the other hand, these acetals are insoluble in the medium in which they are formed, we have here the principle of a method of extraction for the alcohols derived from the sugars, which has long been wanted. The author then goes on to describe a number of experiments with natural mannite, showing the influence on the results of the duration of the reaction, and varying the proportions of mannite, paraldehyde, and hydrochloric acid.

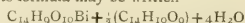
Volumetric Estimation of the Lime and Magnesia simultaneously present in Solutions of Chloride of Sodium. (Waters from Salt Marshes).—Alex. d'Anselme.—Already inserted in full.

On Benzene-ortho-nitrobenzyl Alcohol and its Transformation into Phenylindazol.—P. Freunder.—Already noticed.

The Compounds of Bismuth and Tannin.—Paul Thibault.—During the research the author has been carrying on for some time past, on the compounds of bismuth with the organic acids having phenolic functions, he found it impossible to eliminate, by washing, the mineral acids retained by the compounds of bismuth prepared by double decomposition, or by the precipitation of a salt of the metal by a concentrated solution of the body just used, so he tried another method. Hydrated oxide of bismuth was placed in contact in the cold with a slight excess of tannin; after three days the supernatant liquor no longer contained any tannin; a fresh quantity was added, and after a very prolonged contact (three months), after having made sure that an excess of tannin was present, the material was washed and dried at a low temperature. The product obtained is a yellow amorphous powder similar to bismuthogallic acid, soluble in the mineral acids, soda, and potash, insoluble in the alkaline carbonates and bicarbonates, as well as in neutral solvents. Analysis gives the figures:—

	Calculated for $(\text{C}_{14}\text{H}_9\text{O}_9)_2\text{Bi}_2$		
C	33.64	33.54	33.82
H	2.79	2.83	2.81
Bi	27.35	27.90	27.91
O (by diff.)	36.22	35.73	35.46

Therefore its formula may be written—



without defining either the number or the place of the substituted oxyhydriles. To sum up, tannin only acts on the hydrated oxide of bismuth and not on the anhydrous oxide; the bismuth is substituted for the phenolic hydrogen, leaving the acid function free; tannin or digallic acid in excess, when acting on oxide of bismuth, becomes fixed to the bismuthotoxin formed, in a proportion varying from $\frac{1}{2}(\text{C}_{14}\text{H}_{10}\text{O}_9)$ to $\frac{1}{4}(\text{C}_{14}\text{H}_{10}\text{O}_9)$, according to the duration of the time of contact, and to obtain the product $\text{C}_{14}\text{H}_9\text{O}_{10}\text{Bi}$ only the theoretical amounts of the component parts should be placed in contact.

The Phenolic Urethanes of Piperidine.—M. Bouchetal de la Roche.—The author gives the properties of some new chlorides, bromides, and nitro-urethanes. These bodies were prepared with the object of identifying them with the bodies he expected to obtain directly by reacting with chlorine, bromine, and nitric acid on phenylic urethane. He gives the results of the action of these agents on different urethanes.

The Constitution of the Colouring-matter of Indigo.—L. Maillard.—The hypothesis of two substances, $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$, makes possible the existence of at least nine bodies of the formula $\text{C}_{32}\text{H}_{20}\text{N}_4\text{O}_4$, while only two are known. The theory of the two indogenides of isatin

requires further the previous superoxidation of half the indoxyl, while the other half remains unchanged, and, finally, the dislocation of the pyrrolic nucleus to transform the blue indigo into the red. On the other hand, the author's theory, admitting only a single body C_{16} , and two C_2 —that is to say, just the number of bodies known—accounts for the facts in a much more simple manner.

Action of Sulphur and Selenium on the Bromide of Phenylmagnesium and the Bromide of α -Naphthylmagnesium.—M. Taboury.—The action of oxygen on these organo-magnesium compounds, having been found by M. Bodroux to give a certain number of phenols, the author wished to see whether reactions of a similar character could be obtained with the other metalloids of the same family, leading to the formation of thio-, seleno-, and telluro-phenols. The results of his experiments, which are described at length, show that the expected results were obtained. Following this up, he found that by acting directly on the compound $Mg \leftarrow \begin{smallmatrix} Br \\ X \end{smallmatrix} R$ with an acid chloride, it was possible to obtain the ethers of these thio-phenols and seleno-phenols.

Note on the Use of a New Denaturising Agent for Commercial Alcohols.—M. Cari-Mantrand.—Already inserted in full.

The Detection of the Products of the Contamination of Water by Methyl Sulphurous Violet and Sulphonised Paradiabenzene.—H. Causse.—Already noticed.

Pressure Regulator for Fractional Distillations under Reduced Pressure.—M. Gab. Bertrand.—This paper requires the accompanying diagram to make its meaning clear.

Separator for Fractional Distillation under Reduced Pressure.—M. Gab. Bertrand.—This paper also requires its accompanying diagram.

A New Refrigerating Agent.—MM. Braconnier and C. Chatelain.—Already noticed.

Apparatus for the Estimation of Nitrogen.—R. Marquis.—Requires the accompanying diagram.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 9th inst., The Duke of Northumberland, K.G., President, in the Chair. The Chairman announced that he had nominated the following Vice-Presidents for the ensuing year:—Sir William Abney, K.C.B., Mr. Shelford Bidwell, Right Hon. Lord Kelvin, Dr. Ludwig Mond, Sir Thomas H. Sanderson, G.C.B., Sir Felix Semon, Sir James Crichton-Browne (Treasurer), and Sir William Crookes (Honorary Secretary). The following were elected Honorary Members:—Prof. E. H. Amagat, Prof. L. P. Cailletet, Prof. J. M. Crafts, Prof. E. W. Morley, Prof. E. C. Pickering, Prof. and Madame Curie, Prof. H. L. Le Chatelier, Prof. G. Lippmann, Prof. J. W. Bruhl, Prof. G. H. Quincke, Prof. E. Fischer, Prof. F. W. G. Kohlrausch, Prof. H. Landolt, Prof. L. Boltzmann, Dr. H. Kammerlingh Onnes, Prof. H. A. Lorentz, Dr. G. Lunge, Prof. P. T. Cleve, and Prof. P. Zeeman. The special thanks of the Members were returned to Mrs. Frank Lawson and Sir Thomas Sanderson, G.C.B., for their donations to the Fund for the Promotion of Experimental Research at Low Temperatures. The following were elected Members:—Mr. P. M. Brophy, Mr. W. J. Canter, Mr. Eyre Crowe, Mr. H. T. Ellis, Miss E. Morgan, Mr. Berkeley Portman, and Mr. Burnett Tabrum, J.P.

Institute of Chemistry Examinations.—Pass Lists (April, 1904).—Final A.I.C. Examination—Branch "A" (Mineral Chemistry): James John Ellis, B.Sc. (Vict.),

Yorkshire College, Leeds; Arthur Gordon Francis, B.Sc. (Lond.), Royal Coll. of Science, London, and under S. R. Trotman, F.I.C., and in the Government Laboratory; James Henry Pizey, Assoc. R.C.Sc. (Lond.), Royal Coll. of Science, London, and under Bertram Blount, F.I.C.; Louis John Ezekiel Riley, Univ. of Edinburgh, Glasgow and W. of Scot. Tech. Coll., and King's Coll., London. Branch "B" (Metallurgical Chemistry): Reginald Tyler, Univ. Coll., Nottingham, and under A. H. Allen, F.I.C. Branch "D" (Organic Chemistry): Reginald William Lane Clarke, Finsbury Tech. Coll., London; Oliver Charles Minty Davis, B.Sc. (Lond.), Univ. Coll., Bristol; Bernard Farmborough Howard, Finsbury Tech. Coll., London. Branch "E" (Analysis of Food and Drugs, and of Water, including Examination in Therapeutics, Pharmacology, and Microscopy): Harold Frederick Barke, The Owens Coll., Manchester, and under A. E. Parkes, F.I.C.; Cyril Dickinson, B.Sc. (Vict.), Yorkshire Coll., Leeds, under J. Kear Colwell, F.I.C., and W. Scott Tebb, M.A., M.D., A.I.C.; Ernest Garratt, B.Sc. (Vict.), Univ. Coll., Liverpool, and under J. Campbell Brown, D.Sc., F.I.C., and W. Collingwood Williams, B.Sc., F.I.C.; Charles Edgar Male, School of the Pharmaceutical Society, King's Coll., London, and under Thomas Tickle, F.I.C.; John Robert Stubbs, M.Sc. (Vict.), Univ. Coll., Liverpool, and under J. Campbell Brown, D.Sc., F.I.C., and W. Collingwood Williams, B.Sc., F.I.C.

The Formation of Alloys of Sodium and their Importance in the Phenomena of Cathodic Polarisation.—M. Sack.—Cathodes of lead and of tin are polarised in soda solutions, and the rapid disengagement of hydrogen corresponds with their swelling up, a result caused by the intermediate formation of alloys of sodium on these cathodes. The alloys of sodium with lead and tin, obtained by the fusion of the metals in a porcelain or iron crucible in the presence of hydrogen, have properties varying according to their proportion of the alkaline metal. Alloys of lead with 40 or more atoms per cent of sodium, as well as those of tin with more than 25 per cent, are reduced to powder on contact with water, at the same time giving off hydrogen. It is to the formation of such alloys that we must attribute the attack of the electrodes and their polarisation. The disengagement of hydrogen takes place on lead with an electromotive force of 0.7 volt, and on tin with 0.4 volt. The polarisation of the cathodes take place at potentials of 1.5 and 1.4 volts respectively. Alloys of lead and tin, in alcoholic solution of chloride of lithium cooled down to -80° , have potentials very close to those observed with lead and tin alone. The alloys $Pb_2Na + Pb$ and $Sn_3Na + Sn$ in the cold give the lowest potentials, very close to those of lead and tin, while the alloys $Pb_2Na + Na$ and $Sn_3Na + Na$ give higher potentials. A protective layer is formed on the cathodes which does not occur at the ordinary temperature. When a protective layer is not formed on the alloys poor in the alkaline metal, at the ordinary temperature, we observe a remarkably constant potential, although their composition varies by reason of the disengagement of hydrogen (diminution of the amount of sodium). Measurements made with these electrodes give the same results as those obtained with electrodes of lead or zinc when polarised. Experiments with mercury led to analogous conclusions; with amalgams poor in sodium we obtain a potential identical with that furnished by mercury alone, while amalgams richer in sodium than Hg_2Na diverge in a most distinct manner. At a low temperature, we still observe the formation of a protective layer on the cathode. With platinum and zinc we still observe the swelling of the electrodes, but they do not become reduced to powder. The swelling of the platinum, like that of lead, is much more marked in acid than in alkaline solutions. These facts explain easily why the precipitated sodium soaks into the metallic cathode less easily than the hydrogen, and shows directly that the disengagement of hydrogen at these electrodes is a secondary phenomenon.—*Zeit. Anorg. Chem.*, vol. xxxiv., p. 286.

Accurate Volumetric Apparatus.—Messrs. John J. Griffin and Sons, Ltd., inform us that they are now able to supply volumetric apparatus tested at the National Physical Laboratory. For many purposes for which these vessels are used a certificate of the exact value is not needed; it is sufficient to know that the graduations are correct within some specified limit of error. This knowledge is secured by placing the Laboratory Mark on vessels which come up to the specification. The plan used for limits of error is the one adopted by the "Reichsanstalt," and it is proposed for the future to adopt it at the National Physical Laboratory.

Technics.—This magazine, which is intended as an aid to Technical Progress, is maintaining the promise of the earlier numbers. No. 5, which is the current number, contains articles on Paper Making (Espano), Boot and Shoe Manufacture, Structural Design, Technical Education in America, the Formation of Loops and the Construction of Looped Fabrics, and many others of technical and general interest. Practically all the articles are illustrated, and of these this number contains nineteen, besides reviews, personal items, *Technics* competitions, &c. *Technics* is published by Messrs. George Newnes, Ltd., and is well worth reading, both by manufacturers and others engaged in the various technical industries.

MEETINGS FOR THE WEEK.

TUESDAY, 17th.—Royal Institution, 5. "Meteorites," by L. Fletcher, F.R.S., &c.

Society of Arts, 8. "Pewter and the Revival of its Use," by Lasenby Liberty.

WEDNESDAY, 18th.—Chemical, 5.30. "Action of Nitrosyl Chloride on Pyrene," by W. A. Tilden. "The Electrolytic Estimation of Minute Quantities of Arsenic," by H. J. S. Sand and J. E. Hackford. "The Decomposition of the Alkyl Ureas," by C. E. Fawcett. "The Action of Sodium Methoxide and its homologues on Benzophenone Chloride and Benzal Chloride" (Part II.), by J. E. Mackenzie and A. F. Joseph. "The Formation of Periodides in Nitrobenzene Solution—II., Periodides of the Alkali and Alkaline Earth Metals," by H. M. Dawson and Miss E. E. Goodson. Microscopical, 8. "Note on Grayson's Rulings," by E. M. Nelson. Exhibition of Flower Seeds under Microscopes, by C. Beck.

THURSDAY, 19th.—Royal Institution, 5. "Great Britain and Europe (1763–1793)," by Arthur Hassell, M.A.

FRIDAY, 20th.—Royal Institution, 9. "The Radiation and Emanation of Radium," by Prof. E. Rutherford, F.R.S.

SATURDAY, 21st.—Royal Institution, 3. "Sonata Style and the Sonata Forms" (with Musical Illustrations), by Donald Francis Tovey, B.A.

UNIVERSITY OF BIRMINGHAM.

DEPARTMENT OF METALLURGY.

Applications are invited for the Post of ASSISTANT LECTURER and DEMONSTRATOR in METALLURGY. Stipend £150 per annum. The successful Candidate will be required to commence work on the 1st of September next, to devote his whole time to the duties of the office, and to work under and carry out the instructions of the Professor of Metallurgy. Applications, accompanied by copies of three recent testimonials, should be forwarded to the undersigned on or before Tuesday, May 31st.

Further particulars may be obtained from—

GEO. H. MORLEY,
Secretary.

CITY OF BIRMINGHAM MUNICIPAL TECHNICAL SCHOOL.

The services of an ASSISTANT LECTURER for the CHEMISTRY DEPARTMENT are required from September 1st next.

The commencing salary offered is £125 per annum. The last date for sending in applications is MAY 31st.

Full particulars of the post will be forwarded on application to—
GEO. MELLOR, Secretary.

Offices of the School, Suffolk Street,
May 9, 1904.

RADIUM

ON SALE AND LET ON HIRE.—Write for terms.

The following can be had by return of post.

Pitchblende, direct from Joachimsthal, very radio-active, from 1/- to 30/- per piece.

Itacolumite, or flexible sandstone, 10/- to 25/- per piece (very rare).

Kunzieite, 1/- per gramme. Selected, clear, 2/-

Spartelite (see NATURE, 31/3/04, fol. 523), 2/- and upwards.

Chlorophane, 2/- and upwards **Barium Platino Cyanide in large Crystals** in course of manufacture. (ORDERS BOOKED).

Zinc Sulphide. Phosphorescing a beautiful Green, 2/6 per tube.

Calcium Sulphide " " " Yellow, 2/6 "

" " " Violet, 1/- "

Radio-active Residue from which Radium is made; very scarce, 2/-

Polonium Sulphide, in tubes of one gramme, 21/-

" on Bismuth Rod or Disc, ... 25/-

" on Copper " " " 25/-

Radio-active Screens (Willemite), 6d. per sq. inch. Plat. Bar.

" " " " " Cyan Screen, 9d. sq. inch.

" " " " " (Zinc Sulph.), 10 x 10 cm. 7/6.

Professional Men, Universities, Schools, &c., allowed special terms.

Our newly invented Thorium Inhalers may be had on hire.

ARMBRECHT, NELSON & CO.,
71 & 73 DUKE ST., GROSVENOR SQ., LONDON, W.
Telephone: GERRARD 4942.

N.B.—We have to-day received a consignment of the New Zealand Vegetable Caterpillar; it is from 2 to 3 inches long, with a stem showing fructification growing out of its head. Scientific name of the insect is *Heptalus virescens*; the name of the fungus is *Sphaeria Robertsonia*. Specimens may be had from 10/6 to 21/-, according to quality and size.

TERMS CASH WITH ORDER.

Goods may be returned if not approved of, when money will be refunded.

Cambridge University Press.

BALTIMORE LECTURES ON MOLECULAR DYNAMICS AND THE WAVE THEORY OF LIGHT. Founded on Mr. A. S. HATHAWAY'S Stenographic Report of Twenty Lectures delivered in Johns Hopkins University, Baltimore, in October, 1884; followed by Twelve Appendices on Allied Subjects. By LORD KELVIN, O.M., G.C.V.O., P.C., F.R.S., &c., Emeritus Professor of Natural Philosophy in the University of Glasgow. Demy 8vo. 15s. net.

THE CAMBRIDGE PHYSICAL SERIES.—New Volumes.

RADIO-ACTIVITY. By E. RUTHERFORD, D.Sc., F.R.S., F.R.S.C., Macdonald Professor of Physics, McGill University, Montreal. Demy 8vo. 10s. 6d. net.

SCOTSMAN—"Well informed in its subject, cautious but clear in its statement, and stimulating in its suggestions of new lines of research, the book ought to take a prominent place in the steadily increasing literature of the fascinating physical problems with which it deals."

CONDUCTION OF ELECTRICITY THROUGH GASES. By J. J. THOMSON, D.Sc., LL.D., Ph.D., F.R.S., Fellow of Trinity College, Cambridge, Cavendish Professor of Experimental Physics, Cambridge. Demy 8vo. 16s. TIMES—"Radium and the property of radio-activity presented the physicist with a most abstruse and intricate problem, and, largely owing to the assistance derived from these researches, that problem is now completely solved."

A TREATISE ON THE THEORY OF SOLUTION, including the Phenomena of Electrolysis. By W. C. D. WHETHAM, M.A., Fellow of Trinity College, Cambridge. Demy 8vo. 10s. net.

ELECTRICITY AND MAGNETISM—An Elementary Text-book. Theoretical and Practical. By R. T. GLAZEBROOK, M.A., F.R.S., Director of the National Physical Laboratory, Fellow of Trinity College, Cambridge. Crown 8vo. 7s. 6d.

LONDON: C. J. CLAY & SONS,
CAMBRIDGE UNIVERSITY PRESS WAREHOUSE, AVE MARIA LANE.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2321.

III.

CONNECTION BETWEEN THE VOLATILITY OF COMPOUNDS AND THE CHEMICAL FORCES AT PLAY WITHIN THE MOLECULE.

By GEOFFREY MARTIN, B.Sc. (Lond.).

IN the CHEMICAL NEWS for January 29, 1904 (vol. lxxxix., p. 41), I showed that there exists an intimate connection between the volatility of the fluorides, chlorides, and oxides, and the intensity of the chemical forces which the fluorine, chlorine, and oxygen atoms are capable of exerting.

I propose to give here a brief abstract of a somewhat laborious investigation on this point which I have been engaged in for some time past.

1. Chemically unstable compounds are, as a class, characterised by their volatility and fusibility; chemically stable compounds by their involatility and infusibility.

For example, SiCl_4 , BCl_3 , AlCl_3 , SnCl_4 , &c., are all easy to volatilise and all easy to decompose. The corresponding oxides, SiO_2 , B_2O_3 , Al_2O_3 , SnO_2 , are hard to volatilise and hard to decompose. Indeed, viewed as a class, the metallic chlorides generally are easier to volatilise and easier to decompose than the oxides and fluorides. AgI is less stable than either AgCl or AgBr . It is also more volatile. $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ are characterised by their volatility and by the ease with which they can be decomposed. UO_3 , MoO_3 , WO_3 , CrO_3 , Mn_2O_7 , OsO_4 , RuO_4 are the most volatile and fusible, and at the same time the most unstable oxides of U, Mo, W, Cr, Mn, Os, and Ru. UCl_5 is easier to volatilise and easier to decompose than UCl_4 . WCl_6 is more volatile and less stable than WCl_5 ; MoCl_5 than MoCl_4 ; MoBr_4 than MoBr_3 ; and MoBr_3 than MoBr_2 ; FeCl_3 than FeCl_2 ; CrCl_3 than CrCl_2 ; InCl_3 than InCl_2 ; InCl_2 than InCl ; GaCl_3 than GaCl_2 ; SbCl_5 than SbCl_3 , &c.

The compounds of mercury can be all easily volatilised, and at the same time can be all easily decomposed by heat. The same applies to the ammonium compounds. On the other hand, the compounds of Na and K can neither be easily volatilised nor decomposed by heat in this way.

MgO , CrO , SrO , and BaO are characterised by their great stability and their great volatility; BN is involatile and stable; C_2N_2 is volatile and unstable; the oxides of chlorine, iodine, nitrogen, are all easy to volatilise and easy to decompose; ICl , IBr , ICl_3 , IBr_3 , Se_2Cl_2 , Se_2Br_2 , SeCl_4 , SeBr_4 , S_2Cl_4 , S_2Br_4 , &c., are all volatile bodies, and at the same time easy to decompose. HF is much more stable than HCl or HBr ; it is also much less volatile. HF is a liquid at ordinary temperature, whereas the others are gases.

The vast majority of the carbon compounds are either fluids at ordinary temperatures or become so within a range of 150° . It is the fusibility and volatility of the carbon compounds that is their most striking characteristic; but they are also extremely unstable under the action of heat. Indeed, the whole domain of organic chemistry is destroyed at a red heat.

Similarly the nitrogen compounds are characterised by their volatility and the ease with which they decompose under the action of heat. On the other hand, the silicates, borates, phosphates, metallic carbides, &c., are characterised by their great involatility and their great stability under the action of heat.

Inference.—From these facts we conclude that, statistically considered, there is a connection between the intensity of the

force with which atoms are bound together in the molecule and the volatility of the compounds—the connection being of such a nature that in general the more strongly attracted together are the atoms in the molecule (and therefore the more stable the molecule), the more strongly attracted together are the molecules themselves, and consequently the more involatile the compound.

2. High-grade valency compounds are usually volatile and fusible, low grade compounds involatile and infusible.

There exists a remarkable connection between the valency of an element and the volatility of the compounds to which it gives rise.

Compounds of a high valency grade are usually characterised by their volatility and fusibility, characteristics which become the more conspicuous the higher the type of combination we deal with.

In this connection we may recall to mind the conspicuous volatility of such compounds as $\text{Ni}(\text{CO})_4$, OsO_4 , RuO_4 , Mn_2O_7 , which are all remarkable by reason of their great volatility and fusibility, and because they are the highest types of combination known.

We will briefly recapitulate the chief facts bearing on the matter:— SbCl_5 is more volatile than SbCl_3 ; UCl_5 is more volatile than UCl_4 ; and UCl_4 more volatile than the lower chlorides; WCl_6 and WCl_5 are more volatile than WCl_4 , and this more volatile than the still lower chlorides. FeCl_3 is more volatile than FeCl_2 ; InCl_3 than InCl_2 ; InCl_2 than InCl ; GaCl_3 than GaCl_2 ; and GaCl_2 than GaCl ; CrCl_3 is more volatile than CrCl_2 .

CrO_3 is more volatile than any of the lower oxides of Cr

MoO_3	"	"	"	"	"	"	Mo
WO_3	"	"	"	"	"	"	W
UO_3	"	"	"	"	"	"	U
OsO_4	"	"	"	"	"	"	Os
RuO_4	"	"	"	"	"	"	Ru

Mn_2O_7 is a liquid, whereas all the lower oxides are involatile solids (cf. MnO_2 , Mn_2O_3 , Mn_3O_4 , MnO , &c.); NO_3 is a liquid which does not freeze in a mixture of ice and salt (Berthelot); N_2O_5 is a solid.

All the high-grade compounds of Cr, W, Mo, U, Va, &c., are characterised by their volatility. This tendency is particularly manifest in the multitude of high-grade oxyhalides they produce. The lower grade compounds of the same type are all much less volatile.

High-grade compounds are usually unstable, and it might be thought that this is the reason of their volatility and fusibility (see Part I.).

It certainly does not arise invariably from the greater molecular weight of the lower compounds.

For example, SCL_4 has (as shown by vapour density) a molecular weight of 174, and S_2Cl_2 a molecular weight of 135, yet SCL_4 is much more unstable than S_2Cl_2 . SF_6 boils at -55° , SO_2F_2 at -52° , SOF_2 at -32° , though their molecular weight, as shown by their vapour densities, stand in the ratio 146 : 102 : 86. UCl_5 is more volatile than UCl_4 , though, as shown by their vapour densities, the molecular weights stand in the ratio 477 : 382. The same applies to InCl_3 and InCl_2 , FeCl_3 and FeCl_2 , GaCl_3 and GaCl_2 , CrCl_3 and CrCl_2 , &c., the vapour densities of all of which have been studied.

The reason of the difference in volatility seems to be that the molecules of the lower grade compounds attract each more strongly than the molecules of the higher grade bodies, and so it comes about that the lighter molecules are less volatile than the heavier molecules. It will be remembered in organic chemistry, unsaturated compounds are less volatile than saturated compounds of the same molecular weight.

3. Compounds which react in a very similar way with different reagents usually approach each other closely as regards volatility.

Chemically similar compounds usually approach each other closely as regards volatility. For example, HCl ,

HBr, HI are all chemically similar and all volatile enough to be gaseous at ordinary temperatures, though the molecule of HBr is more than twice as heavy as the molecule of HCl, and that of HI nearly four times as heavy.

Similarly, BCl_3 , SiCl_4 are both volatile liquids; SiO_2 , B_2O_3 , both fixed solids, &c. The general truth of this observation must be apparent to everyone who has even a superficial knowledge of chemistry.

Now the chemical similarity of two compounds arises from the identity of the intensity of the chemical forces at play within the molecule. For example, SiCl_4 and BCl_3 are chemically similar because:—

(a). The B and the Si attract Cl with nearly the same intensity of force.

(b). The B and the Si attract other radicles also with nearly the same intensity of force.

For when the first condition is fulfilled, any influence which is capable of removing the Cl from the one molecule will be capable of removing it from the other; and when the second condition is fulfilled, the B and Si will enter into the same reactions. So that the two molecules BCl_3 and SiCl_4 will, when subjected to the same influences, react in the same way. That, as a matter of fact, in BCl_3 and SiCl_4 the Cl is attached to the B and the Si atoms with nearly the same intensity of force appears from the thermal data:—

$$\frac{1}{2}[\text{B}, \text{Cl}^*] = 34.6 \quad \frac{1}{2}[\text{Si}, \text{Cl}^*] = 39.4,$$

and that B and Si attract not only chlorine but other radicles, such as oxygen, with nearly the same force appears from the data:—

$$\frac{1}{2}[\text{B}, \text{O}^*] = 52.8 \quad \frac{1}{2}[\text{Si}, \text{O}^*] = 52.7,$$

and that chemically similar atomic species in general owe their chemical similarity to the fact that they, in general, attract the same radicles with nearly the same intensity of force likewise appears from a study of thermo-chemical data (I hope shortly to publish a paper on this subject). For example, cobalt and nickel attract the same radicles with nearly the same intensity of force:—

Reaction.	Co.	Ni.
$\text{R} + \text{Cl}_2 + \text{Aq} \dots \dots \dots$	95	94
$\text{R} + \text{Br}_2 + \text{Aq} \dots \dots \dots$	73	72
$\text{R} + \text{O} + \text{Aq} \dots \dots \dots$	63	61
$\text{R} + \text{O}_2 + \text{SO}_2 + n\text{H}_2\text{O} \dots \dots \dots$	163	163
$\text{RCl}_2 + \text{Aq} \dots \dots \dots$	18	19

R stands for either nickel or cobalt; the numbers are the heat evolved by the corresponding reactions (Thomson).

The fact that chemically similar compounds possess nearly the same degree of volatility and fusibility is almost certainly connected with the fact that the chemical forces at play within their molecules are of nearly the same intensity.

It seems therefore that it is the internal chemical forces which the atoms exert on each other in the molecule which decides the external attractive force with which the molecules themselves are attracted together, and therefore the volatility of the compound.

The mere magnitude of the molecular weight has very little influence as compared with the influence of the chemical forces in deciding the degree of volatility. And this is the reason why compounds composed out of very light molecules are often far less volatile than compounds composed of enormously heavier molecules, because the light molecules attract each other with a greater intensity of force than the heavy molecules do.

For example, the molecules of OsO_4 are eleven times heavier than the Na molecules, and yet are enormously more volatile. Compare also H and He, O and F, Hg and Mg, SiF_6 and SOF_2 , &c.; in all these cases the heavier molecules are the most volatile. In fact, the influence of the molecular weight on the volatility only becomes apparent when we eliminate the effect of the chemical forces by considering chemically similar compounds (*i.e.*, compounds in which the chemical forces are of nearly the same intensity).

When we compare chemically dissimilar compounds (*i.e.*, compounds in which the chemical forces at play are of very different intensities), the influence of the molecular weight entirely disappears, and the chemical forces alone decide the volatility.

For example, the replacing of hydrogen in a molecule by Cl or F (atoms 35.5 and nineteen times heavier than H) sometimes leads to an increase of volatility, although the molecular weight is thereby greatly increased (Henri, *Rec. Trav. Chim.*, 1897, xvi., 218, 225), *e.g.*:—

$\{\text{CHCl}_3 \text{ boils at } 61^\circ$	$\{\text{CH}_2\text{Cl}_2 \text{ boils at } 41^\circ$
$\{\text{CFCl}_3 \text{ " " } 24^\circ$	$\{\text{CHFCl}_2 \text{ " " } 14.5^\circ$
$\text{NC} \cdot \text{CH}_2\text{Cl} \text{ boils at } 123^\circ$	
$\text{NC} \cdot \text{CHCl}_2 \text{ " " } 112^\circ$	
$\text{NC} \cdot \text{CCl}_3 \text{ " " } 83^\circ$	

Conclusion.—We therefore conclude that the volatility of any given compound depends almost entirely upon the intensity of the chemical forces with which the atoms which compose it attract other atomic species, and that did we only know the exact intensity of these forces, and the law governing the relation between them and the intensity of the resultant molecular attraction, it would be possible to calculate mathematically the volatility of the compounds, a slight correction being necessary for the gravitational influence of the magnitude of the molecular weight.

Considerations similar to those which lead us to regard the volatility as depending upon the intensity of the chemical forces, lead us to believe that the chemical forces determine also the solubility, fusibility, hardness, &c., of compounds, so that these forces being known the chief chemical and physical properties of the compounds would also be (theoretically) deducible.

Elements are only compounds in which the atoms of the molecule are of the same kind, *e.g.*, O_2 and O_3 are two different compounds composed of atoms of the same kind. Consequently, the same laws which apply to compounds in general apply to elements in particular. Therefore the volatility, fusibility, solubility, &c., of elements themselves in general depend mainly upon the intensity of the forces with which they attract other atomic species, and to a very much smaller extent, upon the magnitude of the molecular weight. A knowledge of these forces would, in fact, give us a very complete picture of all the chemical and physical properties of the elements.

University of Kiel.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1904.

By SIR WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To CHARLES FERRIN, ESQ., M.Inst.C.E.,
Water Examiner, *Metropolis Water Act*, 1871.

London, May 9th, 1904.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 195 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 195 samples examined by us during the month, all were clear, bright, and well filtered.

The deficit in rainfall observed during March has been continued during April. The actual amount of rain registered at Oxford was 0.81 inch; the average rainfall for the month is 1.61 inches; thus we have a deficit of 0.80 inch. This, subtracted from the previous excess of 1.78 inches, leaves an excess for the year of 0.98 inch, or 14.0 per cent above the thirty-five years' average.

Our bacteriological examinations of 354 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 352 others from special wells, standpipes, &c., making 706 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	109
New River, filtered (mean of 69 samples) ..	15
Thames, unfiltered (mean of 23 samples) ..	4798
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 190 samples) ..	19
Ditto ditto highest	136
Ditto ditto lowest	0
River Lea, unfiltered (mean of 24 samples) ..	150
River Lea, from the East London Water Com- pany's clear-water wells (mean of 24 samples)	7

Of the 283 daily samples taken from the general filter wells of the Metropolitan Water Companies, seventeen samples, or 6.0 per cent, were sterile. Only five samples, or 1.7 per cent, contained more than 100 microbes, and of these, none contained as many as 150 microbes per c.c. The five excess samples contained an average of 123 microbes per c.c. In March ten excess samples contained an average of 1.48 microbes per c.c. Thus it will be seen that, chemically and bacteriologically, the general supply is excellent.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

A PRACTICAL METHOD FOR THE ESTIMATION OF OZONE.

By A. BRUNCK.

Some years ago I remarked (*Berichte*, 1900, vol. xxxiii., p. 1832) that the practical methods of estimating ozone could only be based on titration with hyposulphite of iodine set free in a solution of iodide of potassium. Quite recently, Ladenburg (*Berichte*, 1903, p. 115) has examined several other methods for its estimation, based on the use of sulphite and arsenite of sodium, and has found that they give results much less accurate than those obtained by the iodide of potassium method.

It is well understood that ozone behaves very differently with iodide of potassium, according to whether the latter is in acid or neutral solution; that is to say, according as it is in the presence of iodine or of hydroiodic acid. For equal quantities of ozone, and with $N/5$ solutions, the amount of iodine set at liberty is 50 per cent higher in the former than in the latter case.

Chemical literature gives no information on this point; some writers state definitely that the ozone must be made to act on a neutral solution of iodide; others, on the contrary, recommend its previous acidulation to prevent the formation of iodate.

In most cases no importance seems to be attached to this question.

However, in a recent paper, R. Luther and H. Inglis

(*Zeit. Phys. Chemie*, 1903, vol. xliii., p. 203) state that Brodie (*Phil. Trans.*, 1872, vol. clxii., p. 455) observed long ago that ozone reacts very differently with iodide of potassium, according to the conditions of the experiment. Brodie's work has been evidently passed over and forgotten, as it is never mentioned in any of the ordinary text-books, and Englers himself does not mention it in the monograph he has written on ozone.

It is very difficult to determine under which circumstances (in neutral or acid solution) the reaction of ozone on iodide takes place normally. As a matter of fact, on the one hand there was no method of estimation, free from all doubt, until quite lately; and on the other hand, it is not possible to prepare a gaseous mixture containing a known quantity of ozone. In face of this difficulty I consider that hydroiodic acid gives the most exact results; it appears, in fact, that the reaction is extremely simple, and that the only cause of error is the direct oxidation of the hydroiodic acid by the atmospheric oxygen. Now, direct experiment has shown me that this oxidation was absolutely negligible at the strengths at which my experiments were carried out. On the contrary, the action of the ozone on neutral solutions of iodide, seems as if it ought to be much more complex on account of the formation of free alkali, which might bring about secondary reactions and losses of ozone.

Later on, Ladenburg, and R. Quasig (*Berichte*, 1901, vol. xxiv., p. 1184) described a method for estimating ozone by direct weighing. A glass bulb, closed with a tap, is weighed first full of pure oxygen, then full of ozonised oxygen; the difference of these two weights, under the same conditions of temperature and pressure, enable us to calculate the weight of the ozone contained in a known volume of the gas under consideration. Though this method appears to be so simple, yet it is difficult to apply in practice, as many minute precautions must be observed in carrying it out. In spite of this drawback, pointed out by the authors themselves, the method is valuable, as by its means we can check all the others; and, more particularly, we can solve the question of the action of ozone on iodide of potassium.

The numerous experiments made by Ladenburg and Quasig in this direction, have led to an altogether unexpected result. To obtain results agreeing with those furnished by the ponderable method, it is necessary to react with the ozone on a neutral solution of iodide, and only to acidulate the latter at the moment of titration.

I have confirmed my previous experiments by means of the ponderable method, and I am convinced that the conclusions arrived at by Ladenburg are perfectly correct, although they are contrary to all expectations.

The principle of the iodometric method of estimating ozone being known, I directed my attention to its practical application. With this object I constructed a special apparatus, similar to that proposed by W. Hesse (*"Lehrbuch der tech. Gasanalyse,"* C. Winkler, Third Edition, p. 119), for the estimation of carbonic acid in gases containing only a small proportion. It is constructed entirely of glass, in such a manner as to prevent the contact of the gas with any organic substance, indiarubber, cork, &c. All the operations comprising an estimation—the measurement of the volume of the gas, the decomposition of the ozone, the titration with iodine—are all carried out in the apparatus itself.

The apparatus consists of a conical flask of 600 cubic centimetres capacity, closed by means of a hollow ground-glass stopper. This stopper carries a graduated funnel tube, reaching almost to the bottom of the flask, and with a glass tap, A, a little below the funnel; below this tap a side tube is sealed in, serving to introduce the gas; it is also fitted with a tap, B. This tube is fixed in such a position that the liquid running from the funnel cannot enter it. The neck of the flask also carries a side tube sealed in, and the hollow stopper is pierced with a hole, in such a manner that, when this hole is placed opposite a tube, C, the apparatus communicates with the outer air;

knobs of glass sealed on to the stopper serve to facilitate the rotation of the latter in its seat. The capacity of the flask is determined accurately by the weight of water it contains. This capacity is marked on the outside. All the ground parts should form perfect joints, even when dry. If this is not the case, concentrated sulphuric acid must be used as a lubricant, to the exclusion of all fatty substances.

We commence by connecting the apparatus with the source of ozonised gas, avoiding contact of the gas with any organic substance. For this purpose we must use either a ground-glass joint or the hydraulic sealing arrangement devised by Engler and Masse (*Ann. de Chem. et de Phys.*, vol. xciv., p. 225); or again, two brass tubes cemented on to the two glass tubes to be joined, and these are screwed together, making the joint tight with asbestos paper.

If the two tubes to be connected are of the same outer diameter, they may be covered with a piece of glass tube about 2 centimetres in length, of the nearest possible size. The extremities of the two tubes are placed in contact and the covering tube luted on by means of melted paraffin. In this manner we obtain a very good joint, easy to disconnect.

The gas to be examined is passed into the apparatus in such a manner as to completely displace the air it contains. The gas enters through the tube sealed into the funnel stem, and leaves by the lateral tube sealed into the neck of the flask; the taps B and C are open, while A is closed. Once the air is driven out, the tap B is first closed, and then C by a slight rotation of the stopper. If the filling of the apparatus is effected by means of aspiration, it is necessary to proceed in the inverse order. The funnel is filled with a N/5 solution of iodide of potassium, up to one of the graduated marks, and the funnel tap is opened. To make the liquid penetrate into the apparatus, it suffices to place the latter in communication with the outer air for a few instants; this is done by means of the tap C. During this operation a volume of gas is removed exactly equal to the volume of the reagent used, and this must be allowed for in the calculation of results. The absorption of the ozone is almost instantaneous; it gives rise to the formation of white fumes, and even to fumes of iodine, if the proportion of iodine is high; these fumes are rapidly absorbed by frequent agitation. As soon as they have disappeared the stopper is removed and the tubes rinsed, both inside and out, and a quantity of N/10 sulphuric acid added, equal to the amount of iodide used. The iodine set free is titrated with centinormal hyposulphite of soda in the presence of starch. The use of a more concentrated solution of hyposulphite is not recommended because of the instability of such solutions. If the gas under examination contains too great a proportion of ozone, only a known fraction of the iodide liquor is titrated.

It is customary to express the amount of ozone present in grammes per cubic metre of gas. If it is desired to express it in volumes per cent, we take a titrated solution of such a strength that 1 cubic centimetre corresponds to 1 cubic centimetre of supposed gaseous ozone in the normal state. Before making any calculations we must determine the volume of gas on which we have operated, which is done by subtracting from the capacity of the apparatus the volume of the solution of iodide used.

Two pieces of apparatus of the same kind, placed in series and filled with the same gaseous mixture, give perfectly concordant results.

It is just the same if we slowly displace the gas contained in an apparatus by introducing water, and let the gas bubble through two Drechsel washing flasks containing iodide of potassium. From this experiment we may conclude that the time during which the gas is in contact with the iodine is without influence on the completion of the reaction, a result which agrees with that found by K. Garzorzli-Turnlack (*Sitzungsber. d. K. K. Akad. d. Wissensch. Wien*, 1901, cx., II.). It does not matter, as far as the final result is concerned, whether the ozone is

decomposed slowly, by passing it bubble by bubble through a solution of iodide, or whether the whole of the gas is put suddenly in contact with the reagent.

As for the action of the ozone on acidulated solutions of iodide, Ladenburg represents it by the following equation:— $4O_3 + 10HI + H_2O = 5I_2 + H_2O_2 + 5H_2O + 3O_2$.

The formation of peroxide of hydrogen explains the reappearance of the blue colour in the liquid after the titration by hyposulphite.

I have examined the influence of the time of contact, and of the concentration of the hydriodic acid on the reaction. The duration of the time of contact is without any influence, and the concordance of the results obtained with a given acid solution is as close as that obtained when using a neutral solution. But if we use more and more concentrated solutions of hydriodic acid, we find that the amounts of iodine set free increase for a given ozonised gas. With solutions comprised between N/10 and N/5 we obtain 3 atoms of free iodine per molecule of ozone; with a normal solution we obtain 3.7 atoms, and with a double normal solution, 4.2 atoms.

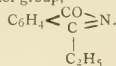
The reappearance of the blue colour in the liquid, after the titration with hyposulphite, which always takes place when the ozone has been passed slowly through a neutral solution of iodine, has never been observed in these experiments. The equation proposed by Ladenburg is therefore at fault in this respect. I have endeavoured to account for the excess of iodine set free in this case by admitting that the ozone exercises a catalytic action on the reaction between the oxygen and the hydriodic acid. This explanation is not plausible, for the excess of iodine set free in a solution of hydriodic acid of given strength, is proportional to the quantity of ozone entering into the reaction, which is contrary to the definition of catalysis.

To explain this particular behaviour, we may make the following supposition. The molecule of ozone decomposes on contact with certain substances, into an atom of very active oxygen and a molecule of inactive oxygen. But this latter possesses, at the moment of its formation, a more powerful oxidising action than that of ordinary oxygen, and it is capable of oxidising certain easily oxidisable bodies, such as hydriodic acid, while it is not able to oxidise other bodies, such as iodide of potassium, ferrous sulphate, or arsenious acid. At the moment when the two atoms do not form a completely closed molecule, we have to deal with a special case of the nascent state.

This supposition is confirmed by the following fact:—When a given quantity of ozonised oxygen is rapidly put in contact with hydriodic acid, the oxidation takes place instantly, and the separation of the iodine, which eventually occurs, is very slight and of the same order as that brought about by contact with pure oxygen.—*Zeitschrift für Angewandte Chemie*, 1903, p. 894.

Action of Mixed Organo-magnesium Compounds on Phthalimide and Phenylphthalimide.—Constantin

Béis.—The author investigates the action of $Mg < \begin{smallmatrix} Br \\ C_2H_5 \end{smallmatrix}$ on phthalimide and phenylphthalimide, and finds that, with the first of these substances, a body is produced which belongs to the isoindol group.—



The Hydrates of Methylene Alcohol and Acetone.—E. Varenne and L. Godefroy.—With methylic alcohol the authors prepare the six hydrates $CH_3OH + H_2O$, $CH_3OH + 2H_2O$, $CH_3OH + 3H_2O$, $CH_3OH + 4H_2O$, $CH_3OH + 5H_2O$, $CH_3OH + 6H_2O$, $CH_3OH + 2H_2O$, and they also find that acetone gives with water at least three definite hydrates, $CH_3-CO-CH_3 + 3H_2O$, $CH_3-CO-CH_3 + 4H_2O$, $CH_3-CO-CH_3 + 8H_2O$, and probably— $CH_3-CO-CH_3 + 34H_2O$.

—*Comptes Rendus*, cxxviii., No. 16.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

CONVERSAZIONE AT BURLINGTON HOUSE.

ON Friday evening last, May 13, 1904, a *Conversazione* was held at the Society's rooms, Burlington House, Piccadilly. The guests, who numbered about 900, were received by the President, Sir William Huggins, K.C.B., O.M., and the members of the Council.

The exhibits were of an interesting character, though there was nothing of a strikingly novel kind such as the Fellows have become accustomed to expect at these functions. Among those which attracted attention were some excellent examples of Microphotography shown by Mr. ARTHUR SMITH and Mr. RICHARD KERR, F.G.S. Their exhibit included sections of histological, botanical, and entomological specimens, intended to assist students of biology generally and medical students especially. The camera used is unusually large in order to ensure direct photography. In no case were the results produced from the enlargement of small negatives.

Some models and photographs of large Hail-stones were shown by the Royal Meteorological Society; some of these fell in Yorkshire, Sussex, and at Montreux in France, and though rare in Europe they are by no means such curiosities in tropical regions.

Mr. J. W. GORDON's exhibit of High Power Microscopy was of interest. The apparatus exhibited consisted of a compounding draw-tube and oscillating screen, as proposed in J. W. Gordon's paper on the Helmholtz theory of the microscope recently read before the Royal Microscopic Society. The object is to get rid of the blemishes in very highly super-amplified images which Helmholtz proved to be due to the extremely small diameter of the Ramsden circle incidental to excessive magnifying power, and it is accomplished by employing an opalescent screen in the view plane of the principal microscope to serve as a secondary source of radiation, and expand the transmitted wave-front. The screen is kept oscillating in order to render its grain invisible. The object exhibited was a diatom (*Pleurosigma angulatum*) magnified about 10,000 diameters.

Prof. J. A. FLEMING, F.R.S., showed an Apparatus for the metrical study of Stationary Electric Waves on Spiral Wires. The apparatus exhibited consists of a long solenoid of silk covered wire having 5000 turns and a total length of 643 metres. This solenoid has parallel to it an adjustable earth wire and a divided scale. The solenoid is connected to one point on an oscillatory electric circuit consisting of a couple of Leydens having a capacity of 0.00068 mfd. and an adjustable inductance of 0 to 230 microhenrys, and a silent discharger. When oscillations are set up in this circuit by induction coil discharges and the frequency adjusted, stationary electric waves are set up in the solenoid. The position of the loops and nodes is ascertained by the use of a series of carbonic dioxide vacuum tubes.

The exhibit of Dr. A. E. WRIGHT was of special interest; it consisted of apparatus and methods employed for measuring, in the case of human blood, its content in agglutinating substances, bactericidal substances, red blood corpuscles, albuminous substances, calcium salts, and salts generally. Of the methods which were exhibited, some are employed in connection with the study of the changes produced in the blood by anti-typhoid, anti-staphylococcus, and anti-tubercle inoculation; others are employed in connection with the determination of the efficiency of the kidney, and in connection with the study of the conditions of blood which are associated with hæmorrhage, serous effusion, and intravascular coagulation.

Dr. A. B. GREEN showed some photographs illustrative of induced Radio-activity of Bacteria; and Mr. H. JACKSON

exhibited some new Phosphorescent Materials illustrating various degrees of response to such exciting influences as violet and ultra-violet light, electric discharge, heat, and friction.

The Cambridge Scientific Instrument Company exhibited a Vibrograph for Recording Vibrations photographically; and a Micro-manometer designed by Mr. R. THRELFALL, F.R.S., for use in conjunction with a Pitot tube and side gauge, to indicate the velocity of gases in pipes or chimneys.

Mr. H. H. CUNYNGHAME, C.B., showed his Improved Muffle and Melting Furnaces at work. The plan on which these furnaces are constructed is to jacket them thickly with non-conducting material, in such a way that heat cannot escape as fast as it is developed, until a high temperature has been attained.

By this plan, muffle furnaces can be heated with from 1 to 4; the amount of gas or petroleum which is required without jacketing, and at the same time evenness of temperature is obtained, and the operator not exposed to heat. The furnaces can be used with petroleum or gas, and as the gas jet for muffles up to 7 inches width is only a single Bunsen burner, no flues are required to carry off the fumes.

During the evening three Demonstrations, with the help of the electric lantern, were given in the Meeting Room. They were by Prof. W. A. HERDMAN, F.R.S., on the Recent Investigation of the Ceylon Pearl Fisheries; Mr. FRANCIS FOX, M.Inst.C.E., who showed Lantern Slides, illustrative of—(1) Operations at the Siplon Tunnel, (2) the Victoria Falls and Gorge of the River Zambesi, and proposed Bridge; and the Hon. C. A. PARSONS, F.R.S., who gave a Demonstration of the Auxetophone, which is an air-operated valve used for a reproducer in gramophones and phonographs, and which replaces the usual reproducing diaphragm in such machines, and the application of this valve to the violin was shown. Selections of music, vocal and instrumental, were played on the auxetophone. The augmentation of the sound by the application of this device was very marked, the increase being from five to eight times that of the ordinary gramophone; there was also a greater fullness of the voice apparent, though in some cases the noise was almost overpowering.

CHEMICAL SOCIETY.

Ordinary Meeting, May 5th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. C. M. Beadnell, C. T. Bennett, and T. U. Walton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. W. Eddington Field, 65, Sutherland Road, Armadale, Melbourne, Victoria, Australia; John Hulme, 3, Albert Terrace, Stockport.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—William Barbour, M.A., B.Sc.; R. H. Durward Benn; Robert Currie Bridgett, M.A., B.Sc.; Ellis Clayton; Robert Steel Finlow, B.Sc.; Harold Sankey Hammond; George Mathieson Horn; Percy Kent Le May; Alfred Mander; Tom Sidney Moore, B.A., B.Sc.; Gerald Oscar Morgan Smith; Laurel Cecil Francis Oldfield; William Davidge Page; Gerald Pinchbeck; Thos. Linton Daniel Porter, B.Sc.; Louis John Ezekiel Riley; Franklin Ernest Robertson; Thomas George Shacklady; Clarence Smith, D.Sc.; Henry Heron Smith; Reginald Harry H. Stanger; Robert de J. Fleming-Struthers, B.A.; Walter Tong.

The PRESIDENT announced that the following persons were proposed by the Council for election as Foreign Members:—Henri Becquerel, Cornelis Loby de Bruyn, Frank Wigglesworth Clarke, Madame Marie Curie, Carl Liebermann, Edward Williams Morley; and stated that, in accordance with By-law II., the ballot for their election would take place at the next meeting of the Society on Wednesday, May 18th.

The PRESIDENT announced that the following letter had been received from Sir Henry Roscoe in reply to the address of congratulation from the Society on the occasion of the celebration of the Jubilee of his Doctorate.

"To the Council and Fellows of the Chemical Society I offer my hearty thanks for the honour they have done me through the President, Professor Tilden.

"Instituted in 1841 for the purpose of stimulating chemical research in this country by the leaders of our science of that day, amongst whom Thomas Graham stands pre-eminent, the influence which the Society has exerted during more than half a century on the progress of English Chemistry has been far greater than its founders could have foreseen.

"During the last fifty years our Science has undergone not one but many revolutions, each one widening and deepening its foundations.

"In this wonderful series of changes, thanks to the zeal and ability of its Fellows, both young and old, the Chemical Society has borne no inconsiderable part, and for its still wider influence and its still greater activity no one has warmer wishes than myself.

(Signed) HENRY E. ROSCOE."

Of the following papers, those marked * were read:—

*72. "The Slow Combustion of Ethane." By WILLIAM ARTHUR BONE and WILLIAM ERNEST STOCKINGS.

The authors have studied (1) the interaction of ethane and oxygen at 250–400°, under pressures of 1.75 to 2.33 atmospheres, in borosilicate glass bulbs (compare *Trans.*, 1902, lxxxi., 536); (2) the oxidation of ethane in contact with a surface of porous porcelain at 400–500°, under reduced pressure, in the circulation apparatus described in a previous paper (*Trans.*, 1903, lxxxiii., 1074); and (3) the slow combustion of ethyl alcohol and acetaldehyde. The main conclusions deduced from the experiments are as follows:—

1. The proportions of ethane and oxygen most favourable to chemical change are equimolecular (1:1), although interaction takes place nearly as rapidly in mixtures containing ethane and oxygen in the ratio 2:1. At all temperatures, ethane is oxidised much more rapidly than is methane, other conditions being equal.

2. When ethane is treated with proportions of oxygen insufficient to oxidise the whole to carbon monoxide and steam, there is no preferential combustion either of hydrogen or carbon. In the absence of secondary phenomena, the interaction is always marked by a diminution in the pressure of the cold products without any deposition of carbon or liberation of free hydrogen.

3. The combustion proceeds in several well-defined stages, among which the following have been distinguished:—

(i.). A primary oxidation to acetaldehyde and steam.
(ii.). A further rapid oxidation of the acetaldehyde to formaldehyde, carbon monoxide, and steam.

(iii.). The final oxidation of formaldehyde to carbon monoxide, carbon dioxide, and steam, which may best be considered as due to two simultaneous interactions:—
i. $\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$; ii. $2\text{CH}_2\text{O} + \text{O}_2 = 2\text{CO} + 2\text{H}_2\text{O}$.

4. The combustion of the hydrocarbon may be accompanied by the following secondary phenomena:—

(i.). Hydrogen or methane, or both, may appear in the products without any liberation of carbon, as the result of the purely thermal decompositions of formaldehyde and acetaldehyde vapours respectively, the latter giving rise to methane and carbon monoxide, whilst the former yields hydrogen and carbon monoxide, although its decomposition is a more complex process than that of acetaldehyde.

(ii.). Small quantities of ethylene and hydrogen may appear in the products as the result of the thermal decomposition of ethane.

(iii.). If the heat liberated during the initial stages of oxidation is sufficient to raise the temperature of the interacting gases to the ignition-point, an explosion takes place, during which the excess of hydrocarbon, and probably also

of aldehyde vapours, is decomposed, carbon and hydrogen being liberated together with some acetylene and ethylene. There is no liberation of carbon below the ignition-point.

5. Although ethyl alcohol has not been detected among the oxidation products of ethane, its absence may be explained by the fact that it is oxidised far more rapidly than is ethane under similar conditions.

6. The view taken of the mechanism of the combustion of ethane is supported by the experiments on ethyl alcohol and acetaldehyde.

*73. "The Action of Radium Rays on the Halides of the Alkali Metals and Analogous Effects produced by Heat." By WILLIAM ACKROYD.

The author has studied the action of γ -rays from radium bromide, in its violet glass tube, on the chlorides of lithium, sodium, potassium, rubidium, and caesium, and deduces the following conclusions:—

1. The colour changes produced divide the compounds into two sub-groups:—I. LiCl, NaCl, and II. KCl, RbCl, CsCl, and in the effects observed: LiCl, white; NaCl, orange; KCl, violet; RbCl, bluish-green; and CsCl, green, each sub-group conforms to the constitutive-colour law (*CHEMICAL NEWS*, 1893, lxxv., 27).

2. The division into these sub-groups is also indicated by their differences of molecular aggregation as expressed by $1/\text{sp. vol.}$

3. There is relative stability of the colours produced while they remain in darkness, and their rate of disappearance or decay in day-light varies with the intensity of the light.

4. The relative expenditure of energy in the γ -rays effecting the colour changes decreases with increase of molecular weight, or, in other words, the sensibility to the action of the γ -rays increases with the molecular weight.

5. When the induced phosphorescence has decayed so as to be no longer visible, it can be revived by invisible heat. In the case of fused lithium chloride, a temperature of 37° is sufficient for the purpose.

6. These various features correspond in many respects with the thermal effects produced in other substances, and the whole of the evidence points to the conclusion that both are physical changes.

*74. "The Mutarotation of Glucose and of Galactose. Solubility as a means of Determining the Proportions of Dynamic Isomerides in Equilibrium." By THOMAS MARTIN LOWRY.

The method formerly described (*Proc.*, 1903, xix., 156), and applied to the case of β -bromonitrocampor, has now been used in order to determine the proportion of α -glucose and of α -galactose in the mixtures of dynamic isomerides which are formed when these sugars are dissolved in alcohol or in water. The solubility of α -glucose in anhydrous methyl alcohol gradually increases in the course of a week in the ratio of 0.53:1, and that of α -galactose in the ratio of 0.50:1. The increment of solubility is due to the formation in solution of the stereoisomeric β -glucose (Tanret's γ -glucose) and β -galactose; when equilibrium is reached, the quantity of sugar in solution is nearly twice as great as when the α -form alone is present, and the stereoisomerides must therefore be in approximately equal proportion and be almost equally stable. This result differs from that obtained by Jungius in the case of the methyl-glucosides, for which the ratio was found to be $\alpha:\beta=3:1$ instead of 1:1.

In a mixture having approximately the composition $\text{EtOH} + \text{H}_2\text{O}$, the solubility of α -galactose was found to increase in the ratio 0.39:1 and in a mixture having approximately the composition $\text{PrOH} + 2\text{H}_2\text{O}$ in the ratio 0.35:1. The decrease of the ratio in the aqueous-alcoholic solutions may be attributed to the presence in the solution, along with the stereoisomeric α - and β -galactoses, of a considerable proportion of the hydrated aldehydic form of the sugar, which is probably an intermediate product in the isomeric change (compare *Trans.*, 1903, lxxxiii., 1316); this conclusion is in harmony with the fact that the rate of

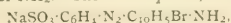
change is many times greater than in the anhydrous methylalcoholic solutions.

Similar experiments were made on the dissolution of α -glucose in mixtures having approximately the composition $2\text{EtOH} + \text{H}_2\text{O}$ and $\text{EtOH} + \text{H}_2\text{O}$, but in each case the gradual increase of solubility was preceded by a more or less rapid decrease owing to the conversion of the solid α -glucose into a less soluble hydrate.

*75. "A Study of the Substitution Products of *ar*-Tetrahydro- α -naphthylamine. 4-Bromo-*ar*-tetrahydro- α -naphthylamine and *ar*-Tetrahydro- α -naphthylamine-4-sulphonic Acid." By GILBERT THOMAS MORGAN, FRANCES MARY GORE MICKLETHWAIT, and HERBERT BEN WINFIELD.

The acyl derivatives of *ar*-tetrahydro- α -naphthylamine (Bamberger and Althaus, *Ber.*, 1888, xxi., 1893), when brominated with one molecular proportion of the halogen or hypobromous acid, ultimately undergo substitution in the aromatic ring, the entrant bromine atom assuming the para-position with respect to the aminic nitrogen. The bromo-base obtained on hydrolysis was shown to be 4-bromo-*ar*-tetrahydro- α -naphthylamine (m. p. 42°) by furnishing successively 1-bromotetrahydronaphthalene and 1-bromodinitrotetrahydronaphthalene (m. p. 91°). The isomeric 2-bromodinitrotetrahydronaphthalene prepared from *ar*-tetrahydro- β -naphthylamine for the purpose of comparison melted at 105–106°. On treatment with diazo-compounds, the bromo-base yields diazoamines of the type $\text{C}_{10}\text{H}_{13}\text{Br}\cdot\text{N}\cdot\text{N}_2\text{X}$. For example, 4:4'-dibromo-1-diazo-1-aminotetrahydronaphthalene prepared by the interaction of the base with its own diazonium salt decomposes violently at 190–194°, and when treated with cold concentrated hydrochloric acid undergoes fission, yielding the hydrochlorides of its generators, the diazonium chloride being identified by the formation of 4-bromotetrahydronaphthalene-azo-3-naphthol (m. p. 215°).

4-Bromo- α -naphthylamine, unlike the analogously substituted tetrahydro-base, condenses with diazo-compounds to form ortho-azo-derivatives having the general formula $\text{XN}_2\cdot\text{C}_{10}\text{H}_7\text{Br}\cdot\text{NH}_2$. The azo-compound,—



yields, on reduction, sulphanilic acid and naphthylene-1:2-diamine.

ar-Tetrahydro- α -naphthylamine-4-sulphonic acid, $\text{NH}_2\cdot\text{C}_{10}\text{H}_{10}\cdot\text{SO}_3\text{H}_2\cdot\text{H}_2\text{O}$, produced by sulphonating *ar*-tetrahydro- α -naphthylamine, was converted into tetrahydronaphthalene-1-sulphonic acid by eliminating its amino-group, the same product being also obtained by replacing this radicle in *ar*-tetrahydro- α -naphthylamine by the SO_2H group and oxidising the tetrahydronaphthalene-1-sulphonic acid thus produced. Tetrahydronaphthalene-1-sulphonic chloride and the corresponding amide melt at 70.5° and 144–145° respectively.

ar-Tetrahydro- α -naphthylamine-4-sulphonic acid differs from α -naphthylamine-4-sulphonic (naphthionic) acid in yielding diazoamino-derivatives and not azo-compounds.

The azo-derivatives of *ar*-tetrahydro- α -naphthylamine were shown to be para-azo-compounds like the corresponding azo- α -naphthylamines, for, on reduction, they gave rise to *ar*-tetrahydronaphthylamine-1:4-diamine.

These results indicate that although *ar*-tetrahydro- α -naphthylamine resembles α -naphthylamine in forming para-azo-compounds with greater facility than a benzenoid amine, yet its para-substituted derivatives, unlike those of α -naphthylamine, do not yield ortho-azo-compounds, and in this respect behave like β -bromoaniline and other similarly substituted bases of the benzene series.

*76. "Studies in the Tetrahydronaphthalene Series. Part II. Halogen Derivatives of *ar*-Tetrahydro- β -naphthylamine. By CLARENCE SMITH.

In a previous paper (*Trans.*, 1902, lxxxi., 900), it was shown that *ar*-tetrahydro- β -naphthylamine resembles primary benzenoid amines in giving diazoamino-com-

pounds, and this resemblance is exemplified further in its behaviour towards the halogens.

Aceto-4-naphthalide yields only 1-bromoaceto- β -naphthalide at the ordinary temperature, even with excess of bromine. *ar*-Tetrahydroaceto- β -naphthalide reacts with one molecular proportion of bromine to form two compounds, namely, 1-bromo-*ar*-tetrahydroaceto-4-naphthalide and 4-bromo-*ar*-tetrahydroaceto- β -naphthalide.

The following compounds have been prepared:—

1-Bromotetrahydronaphthalene, $\text{C}_{10}\text{H}_{11}\text{Br}$, obtained from *ar*-tetrahydro- α -naphthylamine by the Sandmeyer reaction, is a colourless, refractive liquid with an odour resembling that of halogen compounds of the benzene series; it is volatile in steam, and dissolves readily in organic solvents (b. p. 255–257°/751 m.m.).

2-Bromotetrahydronaphthalene, prepared from *ar*-tetrahydro- β -naphthylamine, resembles the preceding compound, and boils at 238–239° under 758 m.m. pressure.

1-Bromo-*ar*-tetrahydroaceto- β -naphthalide, $\text{C}_{11}\text{H}_{11}\text{ONBr}$, resulting from the action of one molecular proportion of bromine on an equivalent quantity of *ar*-tetrahydroaceto- β -naphthalide dissolved in glacial acetic acid, separates from alcohol in colourless, octahedral crystals (m. p. 125.5°).

4-Bromo-*ar*-tetrahydroaceto- β -naphthalide, obtained from the mother liquor in the preparation of the preceding isomeric 1-bromo-compound, separates from alcohol in colourless needles (m. p. 151°).

1-Bromo-*ar*-tetrahydro- β -naphthylamine, $\text{C}_{10}\text{H}_{12}\text{NBr}$, is prepared by hydrolysing the corresponding acetyl derivative; it separates from light petroleum in colourless, silky needles (m. p. 52.5°). It dissolves easily in alcohol or acetone, and is volatile in steam.

4-Bromo-*ar*-tetrahydro- β -naphthylamine crystallises from light petroleum in colourless needles (m. p. 52°); it is not readily volatile in steam.

*77. "Studies in the Tetrahydronaphthalene Series. Part III. Reaction between *ar*-Tetrahydro-3-Naphthylamine and Formaldehyde." By CLARENCE SMITH.

Evidence of the benzenoid nature of *ar*-tetrahydro- β -naphthylamine is obtained from the study of the behaviour of the base towards formaldehyde. The product is methylene-*ar*-tetrahydro- β -naphthylamine, analogous to methyleneaniline. There is no tendency to produce an acridine, which would be evidence of its naphthalenoid character.

The following compounds have been prepared:—

Methylene-*ar*-tetrahydro- β -naphthylamine, $(\text{C}_{11}\text{H}_{13}\text{N})_3$, is obtained together with a polymeric modification, $(\text{C}_{11}\text{H}_{13}\text{N})_x$, when a solution of formaldehyde is added slowly to *ar*-tetrahydro- β -naphthylamine. The trimolecular form separates from acetone or light petroleum as a felted mass of small, white needles; it melts at 121°, and gives an intense blood-red colouration with glacial acetic acid.

The polymeric modification is a white, amorphous powder which, when heated, darkens at 156° and fuses at 164°. It is almost insoluble in acetone, light petroleum, or benzene, but dissolves in hot alcohol, and becomes converted mainly into the trimolecular form.

Methyl-*ar*-tetrahydro- β -naphthylamine, $\text{C}_{10}\text{H}_{11}\cdot\text{NH}\cdot\text{CH}_3$, obtained by the reduction of methylene-*ar*-tetrahydro- β -naphthylamine by sodium and amyl alcohol, is a colourless, refractive, oily liquid which boils at 267.5° under 210 m.m. pressure. The hydrochloride, $\text{C}_{11}\text{H}_{13}\text{N}\cdot\text{HCl}$, crystallises from water in white needles. The nitrate, $\text{C}_{10}\text{H}_{11}\text{N}\cdot\text{HNO}_3$, separates in needles when an ethereal solution of the base is shaken with dilute nitric acid. The nitrosamine, $\text{C}_{10}\text{H}_{11}\text{N}(\text{CH}_3)\cdot\text{NO}$, is a yellow oil, which gives Liebermann's reaction.

*78. "Note on the Hydrolysis of Starch by Diastase." By JOHN SIMPSON FORD.

The writer finds that Kjeldahl's "law of proportionality" is true for the diastase of barley and air-dried malt, as well as for that of kiln-dried malt.

(To be continued)

PHYSICAL SOCIETY.

Ordinary Meeting, May 6th, 1904.

Mr. J. SWINBURNE, Vice-President, in the Chair.

A PAPER entitled "*Some Instruments for the Measurement of Large and Small Alternating Currents*" was read by Mr. W. DUDDELL.

The author, after some preliminary remarks on the available means for measuring alternating currents, proceeded to describe three thermal instruments which he has constructed for this purpose. The first instrument is essentially a sensitive Ayrton-Perry twisted strip ammeter which is very quick in action for a thermal instrument, and has been used for observing and recording P.D.'s and currents which varied as rapidly as one per second. It is compensated for change in the surrounding temperature by forming the sides of the frame which holds the twisted strip with the same wire that the strip itself is made from. With the instrument exhibited a current of 22 milliamperes gave a deflection of one-quarter the scale-distance, i.e., 250 m.m. at one metre scale-distance. The mechanical periodic time is only about one-fiftieth of a second. Using this instrument in series with a high resistance the author has made observations on the variations in the voltages of alternators caused by cyclic irregularity of the engine. By working to a false zero it is easy to obtain 10 m.m. change in deflection for 1 per cent change in the P.D. The second instrument exhibited was a very sensitive thermal galvanometer called in the paper a "Thermogalvanometer." It consists of the combination of a radio-micrometer of the "Boys" type with a very small resistance which is heated by the current to be measured, and which in turn heats the thermojunction of the radio-micrometer by radiation and convection. The principle of its action is as follows:—A loop of wire has its two ends fixed to the two bars of a single thermojunction, a mirror is fixed to the loop, and the whole is suspended in a magnetic field by means of a quartz fibre. The heat from the resistance raises the temperature of the thermojunction, and causes a current to flow round the loop which is deflected by the magnetic field. The sensibility of the instrument depends on the resistance of the heater. Using a heater having a resistance of 13,910 ohms, a deflection of 250 m.m. at a scale-distance of one metre is obtained with a current of 31 microamperes; a heater having 18 ohms resistance required 800 microamperes to give the same deflection. To illustrate the high sensibility of this instrument the author showed the large deflections produced by the currents through a telephone receiver even when the source of sound was many feet distant from the microphone; he also showed that if the thermogalvanometer was placed in series with the vertical receiving wire in spark telegraphy over a short distance, large deflections were produced. The third instrument described was a switchboard instrument which works on the same principle as the last, only that the moving part is pivoted in the usual way. The author exhibited one of these instruments, arranged to give the whole scale deflection for only 0.15 volt, which can be used in connection with shunts to measure large currents; for instance, to measure 1000 amperes the power lost in the shunt would only be 150 watts. Transformers can also be used, as the power to produce the whole scale-deflection is only 0.3 watt. A similar instrument with a high-resistance heater was also exhibited giving the whole scale-deflection for 0.1 ampere, which can be used as a voltmeter by putting resistance in series with it.

Prof. R. THRELFALL, in a letter to the Secretary, congratulated the author on his instruments, and stated that we were not told the effect of change of relative position in the heater and thermojunction during the operation of the thermogalvanometer. This effect might make it possible to construct an instrument having either a scale of equal parts or of any desired form.

Dr. P. E. SHAW, in a letter to the Secretary, said it was

possible to measure the amplitude of vibration in the diaphragm of a telephone-receiver, and Mr. Duddell's instruments would enable us to determine the currents producing these vibrations.

Dr. D. K. MORRIS pointed out that the working forces in an electrostatic instrument could be increased by limiting the angular range without increasing the moment of inertia of the moving system. For instance, this could be effected in a quadrant electrometer with a wide needle by subdividing the needle into narrow fingers, and sub-dividing the quadrants in a similar manner. Dr. Morris showed an instrument constructed on this principle capable of measuring 0.1 volt when used idiosyncratically. The limit to this process of sub-division is decided by the practical working clearance; the clearance being determined by the tilting of the needle due to unbalanced electrostatic forces. Such an instrument may be called a *multipolar electrostatic instrument*, and Dr. Morris has used the same idea in the construction of a *multipolar electrodynamic instrument*. Both of these instruments were exhibited at the meeting. Dr. Morris said he was glad of the opportunity of Mr. Duddell's paper for bringing them forward, and although they were well suited for use as zero instruments as detectors, they were not nearly so sensitive as the instruments designed by the author of the paper.

Prof. W. E. AYRTON said we had another example of the ingenuity of Mr. Duddell, and drew attention to the fact that he had not only designed the instruments but had also constructed them himself. He was pleased to see that good results had been obtained by using an Ayrton-Perry twisted strip. The use of such strips had hitherto been limited by the absence of contrivances for compensating temperature-change effects. With such compensation it is possible by using a twisted strip to combine simplicity of construction with constancy of zero. In expressing especial interest in the experiment on spark telegraphy, Prof. Ayrton referred to the fact that Mr. Duddell had designed his thermogalvanometer for use in an important investigation, being unable to purchase a suitable instrument. The author had spoken about an alternator with a frequency of 120,000, and he hoped we would soon have some account of it.

Referring to the remarks of Dr. Morris, he said it was often difficult to calculate the sensibility of a quadrant electrometer with a divided needle. In order to do so it was essential that the edges of the needles should never be near to the edges of the inductors. Any arrangement to increase the sensitiveness of an electrostatic instrument was desirable, and if Dr. Morris had obtained large deflecting forces without bringing the needles and inductors very near together, he was to be congratulated. He asked the author if it would not be better in his thermogalvanometer to double the heater on itself, and thus obtain a greater heating effect with diminished self-induction.

Mr. A. CAMPBELL expressed his interest in the instruments shown. Some years ago, in connection with the measurement of small alternating magnetic fluxes, he used a hot wire near a minute thermopile connected with an ordinary moving-coil galvanometer. One of the main difficulties with such arrangements was the slowness in reaching a steady deflection and in settling back to zero. For some relative positions of the thermopile and heater the deflection passes through its steady value, and creeps back to it; for other positions the steady value is reached asymptotically. Even in Mr. Duddell's instruments the effect is quite noticeable, and it appears to want further elucidation. In order to render more uniform the calibration of the scale (which normally follows the square law), Mr. Campbell had sometimes mounted the heater so that by its expansion (or that of another hot wire) a spring drew it further from the thermopile as the temperature of the heater rose.

Mr. K. EDGUMBE congratulated the author, and said that as far as small alternating currents were concerned the instruments shown would be very useful. He could not, however, follow the author when he said that his

pivoted form of thermogalvanometer would make a good switch-board instrument, because it was never necessary to measure small currents. In using Mr. Duddell's instruments it was necessary to have very good contacts. Mr. Duddell had spoken of the advantage of being able to remove one heater and put in another, but the speaker pointed out that it would be necessary to adjust the second heater with accuracy, or errors would be introduced. He was not a believer in hot-wire instruments, which were unsuitable for central-station work, and gradually dying out in this country.

Mr. W. A. PRICE said he had recently been thinking of the possibilities of the instrument described by Dr. Watson in the discussion on Prof. Fleming's recent paper on a "Hot-wire Ammeter." He thought that in many respects this instrument would be more practical than those brought forward, although it would probably not be so sensitive.

Mr. W. S. BENNETT asked how far the temperature correction in the twisted strip was perfect. It might be slightly affected by the fact that the twisted strip, though of the same material as the side wires, had been treated rather roughly in the process of flattening and twisting, the coefficient of expansion being possibly lessened. The fact that the strip and wires were at different temperatures might also affect the correction adversely on account of the temperature variation of elasticity. The sensitiveness of the radio-micrometer form of instrument would be increased if the efficiency of heat-transference between the heater and the thermojunction could be improved. If it were possible to make a heater that would nearly surround the junction this might be effected, and the variation of sensitiveness due to inaccurate replacement of the heater after removal would be lessened. He suggested using as a heater a thin film of platinum deposited on the inside of a small thin tube of glass or quartz.

Mr. R. S. WHIPPLE said he would like to testify to the great patience of Mr. Duddell in overcoming the difficulties met with in the construction of his instruments. He was of the opinion that a good deal of the bad name of hot-wire instruments could be attributed to their inability to stand overload.

Mr. H. TINSLEY, referring to Prof. Ayrton's remarks about the position of the needle in an electrostatic instrument, said he had recently tested the matter accurately. So long as the edges of the needle were well within the inductors it was easily possible to calculate the deflection which would be produced by any voltage to about one part in five hundred. Under such conditions the instrument accurately followed a square law, and its working-constant could be obtained from one observation.

The CHAIRMAN said that a thermopile had been used many years ago in a similar way to that in which the thermojunction had been used by Mr. Duddell, but the sensitiveness obtained was not nearly so great as that of the instruments exhibited. With regard to electrostatic instruments he did not see any advantage in being able to predict the deflection produced by any voltage, according to a definite law, as it was always easy to calibrate such instruments. The shape of an instrument with an Ayrton-Perry twisted strip often rendered it unsuitable for many purposes.

Mr. W. DUDELL, in reply, said that it was necessary that the heater and the thermojunction should be very small, and this made it difficult to diminish the self-induction of the heater by doubling it on itself. It was also essential that the bars of the thermojunction should be narrow, otherwise creeping effects were introduced. The deflection might also be too small, due to the increase in resistance of the whole circuit brought about by the heating effect of the current. Referring to Mr. Edgcombe's remarks, he pointed out that his pivoted instrument used less watts than any instrument on the market, and could be used if necessary in connection with transformer instruments.

Mr. F. E. SMITH exhibited and described the following instruments from the National Physical Laboratory:—

1. A mercury-resistance standard.
2. A 10-ohm build-up resistance-box.
3. An astatic galvanometer.

An "Experiment with Lubricating Oils," by Mr. W. A. PRICE, was postponed.

NOTICES OF BOOKS.

Imperial University of Tokyo: The Calendar 1903-1904.
Tokyo: Published by the University. 1904. Pp. 243 + 108.

THIS Calendar contains full information of all kinds concerning the University of Tokyo, commencing with an historical summary and the events leading to the founding of the University. This University is of no great antiquity, for it practically came into existence in March, 1886, though what has been called the "awakening" of Japan was some thirty years earlier.

The course of instruction includes practically every modern subject, and we have had recently, and are still having, striking evidence of the thorough manner in which our friends the Japanese attend to detail; we may therefore be certain that the peaceful arts receive equal care and attention.

Cyaniding Gold and Silver Ores: a Practical Treatise on the Cyanide Process. By H. FORBES JULIAN and EDGAR SMART, A.M.I.C.E. With numerous Illustrations and Working Drawings in the Text, and 35 on Folding Plates. London: Charles Griffin and Co., Ltd. 1904. Pp. 405.

THE cyanide process being comparatively new, textbooks, which can be also looked upon as works of reference, are rather rare; much information on the subject has been published from time to time, but it is so scattered among various periodicals all over the world as to be practically inaccessible to the busy man.

In this volume the authors have brought together a great deal of fragmentary information which has appeared from time to time in books, periodicals, and the transactions of learned societies, and have arranged it in such a form as to make a complete story of cyaniding from its earliest beginnings to its latest developments. That they are well qualified for this task is evident to anyone who reads this book. Practice and theory have been made to go hand in hand, so that the mill manager, while finding numerous hints and much detailed information of a practical kind, will be also led to exercise his reasoning powers through studying the principles involved in the working of the process and the construction of the plant.

The book is divided into forty-four chapters, the first four being on preliminary investigations; without going through them *seriatim* we may point out that all the operations involved in the complete working of the process are taken in order. Crushing, measuring, leaching, solution, precipitation and cleaning up, refining and smelting, each have their own section, besides numerous other chapters for the discussion of the side issues involved, such as the effects of temperature, concentration (a very important point), the absorption of air by solutions, sources of loss of cyanide, &c.

The above mentioned chapters deal with the direct extraction of gold from the crushed ores; there is, however, another most important source of gold recovery which was for many years entirely overlooked; we refer to the recovery of gold from slimes.

Naturally, the gold present in slimes is in an extremely finely divided state, and can be extracted only by getting it into solution. The principles and practice of the mani-

pulation involved in this operation are next carefully gone into.

We then come to chapters on the design and construction of the cyaniding plant, the vats, pumps, laundries, precipitation boxes, &c., the details of which have to be considered and modified at almost every mine. Finally, the cost of cyaniding is fully considered, both as regards capital outlay and maintenance and cost of treatment.

On all these matters the authors speak with authority, as besides being theoretical and scientific experts, they have the additional and equally great advantage of many years of practical work and close connection with other well-known men in the same field, and can add the knowledge of experience to that acquired by study.

Radium and all About it. By S. BOTTONE. London: Whittaker and Co.

THE interest surrounding the discovery and properties of radium is so general that a pamphlet of this character, written for the lay public, is likely to be largely read by those who have neither time nor opportunity to follow the strictly scientific journals. So much nonsense has appeared in print about radium that we welcome a work of this character as a real effort to put the facts concerning one of the greatest discoveries of the century simply and clearly before the public.

Commencing with the observation and properties of cathode rays, and the work of Lenard and Röntgen, the main facts of the discovery and properties of radium and its companions are collected and condensed into small compass. As yet we have no knowledge of the properties of pure radium; all that is known of the element has been gained by a study of exceedingly small quantities of its compounds, chiefly the chloride and bromide; and this fact is kept in mind when discussing, later on, the theoretical considerations involved in the discovery. The note in this connection is worth quoting in full:—"The fact is, that the amount of radium, even in the form of bromide, chloride, or nitrate, at our disposition, has been, up to the present time, so minute that it is premature to build up any theory which, when we can experiment upon pure radium in an uncombined state on a larger scale, may have to be greatly modified, if not altogether discarded. The very fact that not only helium but oxygen, hydrogen, carbon dioxide, and nitrogen are found included in radium bromide, shows how essential it is to the solution of the problem that a fair quantity of pure radium should be experimented upon before any satisfactory theory can be formulated."

Unfortunately, in a compilation of this character, repetitions and the record of erroneous conclusions appear to be unavoidable; and it is a pity that Sir W. Huggins's early statement, that the phosphorescence spectrum of radium bromide gave the helium bands, is quoted, especially as upon this conclusion the author indulges in a good deal of theoretical detail as to the breaking up of the radium atom into that of helium. Later on, the further communication is quoted, showing that the nitrogen and not the helium spectrum is given by the phosphorescence of radium bromide; and that, in so far as this observation is concerned, it gives no support to the alleged transmutation of radium into helium. In this connection, the following quotation from Prof. Rutherford is worth keeping in mind:—"The interpretation of experimental results of such great importance on the transformation theory must naturally be accepted with reserve, until it is proved beyond doubt that the helium present in radium is continuously produced from itself by that element, and cannot be derived from an external source."

On the whole, the main facts about radium are clearly stated, and the book may be commended as an attempt to set out all that is known about one of the most noteworthy victories of patient investigation in such a way that the general reader can form a true idea of the matter.

CORRESPONDENCE.

THE CAMPHOR MONOPOLY IN JAPAN.

To the Editor of the Chemical News.

SIR,—The Japanese Government, who in the latter portion of last year decided to monopolise the camphor industry of that country, are now well on the way towards reaping a rich harvest as the result of it, and therefore the following remarks may prove interesting:—

The total output of camphor and camphor oil in Japan a few years ago was, roughly speaking, 1,200,000 kin—or, in the English equivalent, 1,600,000 lbs.—but this has increased to such an extent that, in the year 1901, it reached a total of five and a-half millions kin, or 7,333,334 English pounds.

The world's total consumption of camphor alone amounts to five million kin or about seven million pounds per annum, and of this over four-fifths is supplied by Japan and Formosa. The actual amounts supplied by these two countries in the years 1899 to 1902 being as follows:—

1899		2,758,625	kin, or	3,678,134	lbs.
1900		3,280,815	" "	4,375,420	"
1901		4,165,757	" "	5,554,342	"
1902		3,953,211	" "	5,270,948	"

From these statistics, it will be seen that a monopoly on camphor, which has now been directed by the Government of the Rising Sun, will do much to better the condition of their finances without any actual taxation of the people themselves. It is estimated in official circles in the Orient that, by this monopoly alone, without affecting the price of camphor to any material extent, the Japanese Government will realise annually a sum of 3,000,000 yen, or, in English money, about £300,000 sterling, which will be used to relieve the rates.—I am, &c.,

STANLEY ROE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 16, April 18, 1904.

Presence of Argon in the Gases of the Hot Springs of Guadeloupe.—H. Moissan.—The author examines two specimens of gas from the hot springs of Guadeloupe, and finds that they are volcanic in character, containing completely combusted carbon products, owing to the admixture of air. Fouqué showed the same thing in the gases from eruptions of Santorin. The small quantity of sulphuretted hydrogen which remains in the gas in both cases either escapes combustion by reason of the excess of water vapour in which it is dissolved, or exists as the result of secondary reactions which take place at a high temperature in presence of water vapour.

Action of Silicon on Water at a Temperature of 100°.—H. Moissan and F. Siemens.—If pure amorphous or crystalline silicon, reduced to a fine powder, is placed in a little glass tube containing distilled water, and the whole brought to a temperature of 95° and left for some hours, decomposition of the water takes place, with production of silicon hydride.

Apparent Diminution of Energy of a Dilute Acid in presence of a Neuter Salt of this Acid.—G. Cheneau.—The production of an alkaline sulphide by the action of H₂S on sodium acetate, even in presence of free acetic acid, is the cause of the apparent dilution of the latter, and of the non-precipitation in presence of acetic acid, even of the same concentration. It is therefore not

necessary to employ the theory of electrolytic dissociation to explain these phenomena.

Spectrum of Zinc.—Maurice Hamy.—The author measures certain of the lines in the zinc spectrum, and compares them with the numbers obtained by Perot and Fabry. The agreement is very satisfactory.

	Hamy	Perot and Fabry
1	0.6392336	0.6392345
2	0.5181974	—
3	0.4810533	0.4810535
4	—	0.4722104
5	0.4680138	0.4680138
6	0.4629810	—

Methylic Ether of Acetol, $H_3C-CO-CH_2(OCH_3)$.—Louis Henry.—The author employs the reaction of methylic alcohol on pyruvic formate, $H_3C-CO-CH_2(CHO_2)$, to evolve a method for the preparation of the acetol $H_3C-CO-CH_2(OH)$,—an alcoholic compound which has hitherto only been obtained with great difficulty by the ordinary methods of saponification of the ether salts. This method of preparation is also interesting from a theoretical point of view.

Methyl Acetolate.—André Kling.—Methyl acetolate, $C_2H_5O-O-CH_3$, can be obtained, not only by the action of dry CH_3OH on acetol formate, but also by the direct reaction of these two alcohols on one another. One part of acetol and two parts of pure and dry methylic alcohol are heated together at 140° for eight or nine hours, and the crystalline product is then obtained by simple evaporation. When prepared by either method, the product is completely purified by two crystallisations from boiling chloroform. The author further examines its properties and physical constants.

Halogen Ether Oxides, $RO(CH_2)_nX$: their Magnesium Compounds, $RO(CH_2)_nMgX$. New Synthesis in the Tetramethylene Series.—J. Hamonet.—Up to the present time those bipyrimaly halogenated ether oxides, $RO(CH_2)_nX$, in which n equals 1, 2, or 3, have never been prepared. The author succeeds, however, in preparing certain of their superior homologues by a method which may be found capable of generalisation.

A New Reaction of Aldehydes.—L. J. Simon and A. Conduché.—The action of acetylacetic ether on aldehydes in presence of ammonia led Hantzsch to evolve a method of synthesis in the pyridic series. More recently, Guareschi undertook parallel researches on the derivatives of glutamic imide. In the same manner, oxalacetic ether condenses with aldehydes in presence of ammonia, giving substitution derivatives of ketopyrrolidone. When benzylic aldehyde is used, a substance with formula $C_{13}H_{13}NO_4$ is formed. The author examines its properties and prepares its potassium, ammonium, silver, and copper salts.

Chloruration of Phenyl Carbonate in presence of Antimony Chloride.—Et. Barral.—For the chloruration of phenyl carbonate the author uses a mixture of anhydrous aluminium chloride and antimony pentachloride. The reaction takes place very slowly in the cold, but more rapidly on heating, the liquid becoming blackish. The chloruration stops after the formation of trichlorophenyl carbonate.

Action of Sulphur and Selenium on Organo-magnesium Compounds of Mono- and Di-halogen Aromatic Hydrocarbons.—F. Taboury.—The author examines the action of sulphur and selenium on organo-magnesium compounds of mono-, bromo-, and di-halogen aromatic hydrocarbons, and finds the reaction similar to that investigated by M. Bodroux on the action of oxygen on these compounds. He finds that, at the same time as thio- and seleno-phenols, a more or less quantity of disulphide or diselenide is also produced, proving that the compounds formed during the reaction are oxidised. The author tabulates the compounds formed and their fusing-points.

Purification and Identification of Alcohols.—L. Bouveault.—The purification and identification of alcohols

is rendered more difficult by the fact that these substances are nearly always liquid and have very few crystalline compounds. The author obtains crystalline derivatives of the various alcohols by preparing the pyruvic ethers. These can be easily purified and identified.

Two Isomeric β -Methylcinnamic Acids.—M. Tiffeneau.—In a previous paper the author describes the preparation of the two β -methylcinnamic acids by the action of CO_2 on the magnesium derivative of α -methyl- ω -bromostyrolene. He succeeds in separating the two acids, owing to their difference of solubility, either in petrol ether or in carbon disulphide. By repeating the crystallisations, he obtains finally two acids of fusing-points 129° and $97-98^\circ$. These two acids may be considered as isomers of position—one being phenylcrotonic acid, $CH_3-C(C_6H_5)=CH-CO_2H$, and the other a phenyl-isocrotonic acid, $CH_2=C(C_6H_5)-CH_2-CO_2H$.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, May 24, at 5, Mr. H. F. Newall begins a course of two lectures at the Royal Institution on the "Solar Corona"; on Thursday, May 26, at the same hour, Mr. H. G. Wells will deliver the first of two lectures on "Literature and the State"; and on Saturday, May 28, at 3 o'clock, Sir Martin Conway begins a course of two lectures on "Spitsbergen in the Seventeenth Century." The Friday Evening Discourse on May 27 will be delivered by the Prince of Monaco, on the "Progress of Oceanography"; and on June 3 by Prof. Svante Arrhenius, on the "Development of the Theory of Electrolytic Dissociation."

"The Times" Engineering Supplement.—*The Times* is so big that nobody, in a general way, has time to read it all; still it contains many articles and letters which should, and would, be by no means overlooked if due attention were drawn to them. By the publication of the "Engineering Supplement" the Editor of *The Times* is bringing this subject nearer to the class of readers for whom it is primarily intended, and we have no doubt that this progressive policy will be appreciated, and will meet with the success it deserves. Engineering is the backbone of English prosperity, and every help it receives is bound to have effect by increasing efficiency, and thus benefiting the country at large.

Silicic Acid (I).—E. Jordis and E. H. Kanter.—By means of measurements of conductivity the authors have arrived at the following conclusions:—The existence of the silicates such as $SiO_3H(NH_4)$ and $SiO_3(NH_4)_2$ may be considered as certain, that of the silicate $SiO_4(NH_4)_3H$ remains doubtful. By double decomposition between the alkaline silicates (silicate of soda) and the alkaline earth salts (Ba, Sr) we obtain precipitates in which the proportion of alkali diminishes with the dilution of the solutions. In the compounds obtained we cannot admit of an isomorphous replacement of the alkaline earths by the alkali. The authors have obtained well-defined compounds by reacting with silica on saturated solutions of baryta water, lime water, or strontium water, at boiling temperature. With a solution of silicic acid containing 1.8 per cent of SiO_2 and baryta water, we obtain a crystalline powder containing $SiO_3Ba.H_2O$. Strontium gives the crystalline salt $SiO_3Sr.H_2O$, and lime a similar compound of $SiO_3Ca.H_2O$, of which the crystalline form has not been proved in a satisfactory manner. By making use of a silicic acid jelly, and the same solutions of $Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ we obtain the same compounds; whatever the excess of alkali used may be, we can only obtain the metasilicates SiO_3M_2 . If we operate in the presence of an excess of acid, we only obtain precipitates of undeterminate composition. By proceeding in the dry way the authors have not been able to obtain sharply defined compounds.—*Zeit. Anorg. Chem.*, vol. xxxiv, p. 455

MEETINGS FOR THE WEEK.

- TUESDAY, 24th.**—Royal Institution, 5. "The Solar Corona," by H. F. Newall, F.R.S., &c.
- THURSDAY, 26th.**—Royal Institution, 5. "Literature and the State," by H. G. Wells, B.Sc.
- FRIDAY, 27th.**—Royal Institution, 5. "Progress of Oceanography," by His Serene Highness Albert Prince of Monaco.
- Physical, 5. "The Law of Action between Magnets and its Bearing on the Determination of the Horizontal Component of the Earth's Magnetic Field with Unifilar Magnetometers," by Dr. C. Chree, F.R.S. "On the ascertained Absence of Effects of Motion through the Ether in Relation to the Constitution of Matter on the Fitzgerald-Lorentz Hypothesis," by Prof. J. Larmor, Sec.R.S. "Coherence and Re-coherence," by Dr. F. E. Shaw and C. A. B. Garrett.
- SATURDAY, 21st.**—Royal Institution, 3. "Spitsbergen in the Seventeenth Century," by Sir William Martin Conway.

CITY OF BIRMINGHAM
MUNICIPAL TECHNICAL SCHOOL.

The services of an ASSISTANT LECTURER
for the CHEMISTRY DEPARTMENT are required from September 1st next.

The commencing salary offered is £125 per annum. The last date for sending in applications is May 10th, 1904.

Full particulars of the post will be forwarded on application to—

GEO. MELLOR, Secretary.

Offices of the School, Suffolk Street,
May 9, 1904.

UNIVERSITY COLLEGE of SOUTH WALES
and MONMOUTHSHIRE, Cardiff.

The Council of the College invite applications
for the following Posts:—

1. ASSISTANT LECTURER in MATHEMATICS.
2. DEMONSTRATOR and ASSISTANT LECTURER in CHEMISTRY.
3. DEMONSTRATOR and ASSISTANT LECTURER in PHYSICS.
4. DEMONSTRATOR and ASSISTANT LECTURER in PHYSIOLOGY.
5. DEMONSTRATOR and ASSISTANT LECTURER in BOTANY.

In the case of the appointment in Physics, preference will be given to candidates who have some knowledge of the technical applications of Electrical Science.

Further particulars may be obtained from the undersigned, to whom applications, with testimonials (which need not be printed), must be sent, endorsed on the outside with the title of the Department in which the application is made, on or before MONDAY, JUNE 20th, 1904.

J. AUSTIN JENKINS, B.A.,
University College, Cardiff, Registrar.
May 16, 1904.

THE CHEMICAL NEWS
AND
JOURNAL OF PHYSICAL SCIENCE.

Published every Friday. Price 4d Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

Five lines in column (about 10 words to line)	£ s. d.
Each additional line	0 3 6
Whole column	0 6 0
Whole page	1 15 0
	3 0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION,
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.

LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery

RADIUM
ON SALE AND LET ON HIRE.—Write for terms.

The following can be had by return of post.
Pitchblende, direct from Joachimsthal, very radio-active, from 1/- to 30/- per piece.
Itacolomite, or flexible sandstone, 10/- to 25/- per piece (very rare).
Kunzite, 1/- per gramme. Select 1, clear, 2/-
Spartelite see NATURE, 31/3 04, fol. 523, 2/- and upwards.
Chlorophane, 2/- and upwards Barium Platino Cyanide in large Crystals in course of manufacture. (ORDERS BOOKED).
Zinc Sulphide. Phosphorescing a beautiful Green, 2 6 per tube.
" " " Yellow, 2 6
Calcium Sulphide " " Violet, 1/-
Radio-active Residue from which Radium is made; very scarce, 2/- tube.
Polonium Sulphide, in tubes of one gramme, 21/-
" on Bismuth Rod or Disc, ... 25/-
" on Copper " " 25/-
Radio-active Screens (Willemite), 6d. per sq. inch. Plat. Bar. Cyan Screen, 9d. sq. inch.
" " (Zinc Sulphide), 10 x 10 cm. 7/6.

Professional Men, Universities, Schools, &c., allowed special terms.

Our newly invented Thorium Inhalers may be had on hire.

ARMBRECHT, NELSON & CO.,
71 & 73 DUKE ST., GROSVENOR SQ., LONDON, W.

Telephone: GERRARD 4942.

N.B.—We have to-day received a consignment of the New Zealand Vegetable Caterpillar; it is from 2 to 3 inches long, with a stem showing fructification growing out of its head. Scientific name of the insect is *Heptamelis virescens*; the name of the fungus is *Sphaeria Robertiana*. Specimens may be had from 10/6 to 21/-, according to quality and size.

TERMS CASH WITH ORDER.

Goods may be returned if not approved of, when money will be refunded.

E. GEORGE & SONS,
BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.

Are OPEN to PURCHASE Complete Sets

or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1850, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.

BRYAN CORCORAN Lim.

MILLSTONE BUILDERS,

WIRE WEAVERS, MACHINE MANUFACTURERS, AND
GENERAL MILL FURNISHERS.

Sole Makers of MILBURN'S

Patent Conoidal Stone Grinding Mills.

Especially suitable for certain materials, Water Dry.

Works and Warehouses: Back Church Lane.

Parcel Dept.: Basement of the Core Exchange.

31, MARK LANE, LONDON.

LIVERPOOL, Rodney Street neighbourhood.
—Large new Premises, suitable for Wholesale Chemist and Druggist Warehouse.—Apply, T. Price, 77, Lord Street, Liverpool.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC,
As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET
LEAD and PIPE, LITHARGE, &c.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2322.

ON THE DISTRIBUTION AND SPECTRA OF METALLIC VAPOURS IN ELECTRIC SPARKS.

By HUGH RAMAGE, B.A., St. John's College.

Some peculiarities observed in certain lines in the arc and spark spectra of lithium were described by the writer in a paper communicated to the Royal Society in November, 1902 (*Proc. Royal Soc.*, lxxi., p. 164). The blue line, for instance, was found to be broadened in the spectra of the regions near the negative element both in the arc and spark. The broadening of this line was easily observed and photographed in the spectrum of the spark when no Leyden jar was used, and a slight broadening was observed near the positive electrode when no air break was inserted in the secondary circuit and no precautions were taken to keep the electrodes cool. Between these two regions the line was thin and sharp. A further study of electric sparks in air at ordinary pressures has since been made and the results will now be described.

Two clean platinum wires were fixed horizontally in a holder with their adjacent ends about a centimetre apart. When they were connected with an induction coil and the coil was started, the flame surrounding the sparks had the characteristic colour due to the gases of the atmosphere. The anode was then moistened with a solution of a compound of lithium and the coil again started. Flashes of red were observed in the sparks, but when the anode was heated the flame round the sparks became red throughout its whole length, and there were seen in its spectrum the red lithium line and the yellow sodium lines. It would appear from this that some of the lithium and sodium, present as an impurity, were vapourised by the heat and reduced to the free state by the spark, otherwise, according to Gouy's observations (*Comptes Rendus*, lxxxiii., p. 70), no colour should be communicated to a flame in presence of so much free oxygen. A quantity of lithium salt was then fused on the end of one of the wires, forming a globule about 2 m.m. diameter. When the coil was started with this as the anode the red flashes were more frequent and brighter than before, and the orange line of lithium was also observed in the spectrum, but it was extremely feeble. When an air break was inserted in the secondary circuit no red colour was observed as long as the anode remained cold.

On reversing the spark, thus making the globule of lithium compound the kathode, a bright red colour developed in the flame near the kathode, but it did not pass the whole way across to the anode unless the electrodes were brought nearer together.



The appearance of the spark and flame is shown in the figure. There were observed in the spectrum of the red portion, viewed through a vertical slit, the red lithium line as a long line, the orange line as a short line of feeble intensity, and the sodium lines as lines of medium length. The orange line is the strongest line in the subordinate series of lithium, and it is only seen near the central axis of the spark. An exceedingly bright spot of white light

was always observed on the salt where the spark touched it, and in the spectrum of this spot the red lithium line and the yellow sodium lines were somewhat brighter than they were in the red portion of the flame, but the lines of the two subordinate series of lithium were exceedingly bright. It was this spot, and possibly the vapour very close to it, which gave the broadened lines in the diffuse series which were described in the above-mentioned paper. The salt on the kathode becomes hot and sometimes it fuses; if the current is then reversed the flame becomes coloured throughout its whole length, but the colour fades away as the temperature of the bead falls. A single spark passing to the kathode produces both the bright spot and the red flame.

The electrodes were next placed vertically in a line, the bead of salt being first placed on the lower end of the upper electrode. When this was made the kathode, the red colour appeared, but it only extended for about one-half the distance from the electrode that it did when these were horizontal; the upward current of hot air from the spark evidently opposed its motion downwards. The bead and electrodes were allowed to cool and the sparks were then passed in the opposite direction, but no red colour appeared until the bead became heated by the upward current of hot air, and then the red colour appeared and extended down to the clean kathode.

The bead was next put on the upper end of the lower electrode. When it formed the kathode the red colour extended up to the anode, but it was deepest near the kathode. When the electrodes were cold and the bead was made the anode no red colour appeared in the spark.

The lithium vapour liberated from a hot anode would appear to carry a positive charge and thus convey part of the current to the kathode, but the lithium vapour liberated from the kathode does not appear to be charged. In no case has it been observed to be repelled by the anode, and it certainly does not appear to be attracted by it; if it is charged negatively at first the charge must be quickly lost. The lithium would appear to be liberated in definite quantity by each spark, in a very short interval of time, but there is no decisive evidence given by these experiments to show whether the vapour passes away in an explosion wave or merely by diffusion in the gases heated to a high temperature by the passage of the spark. Sodium vapour passes about as far from a kathode of sodium salt as lithium does; this is in favour of the former view.

There is evidently an intense chemical action taking place in the bright spot on the kathode, and there seems no doubt but that lithium is liberated from combination by electrical action at this point. It is probable that the production of the subordinate series is associated with the process of liberation of the metal, that the vibrations producing the lines of these series are peculiar to the atom at the moment of its liberation, perhaps to the atom and the electric charge then given to it, whilst the vibrations producing the lines of the principal series are peculiar to some change, combination or otherwise, of the free atom of the metal. The lines of the subordinate series become broader and apparently brighter as the negative pole of the arc is approached, and this pole, according to Violle, has a temperature of about 2700° when the positive pole is about 3500°, and the temperature of the arc itself is still higher. The apparent brightening of the lines is not a temperature effect.

The results obtained with a compound of sodium are similar to those obtained with lithium. Potassium gives a different result when a bead of its carbonate is on the kathode. There is no flame near the kathode, the spark is reduced to a thin line, whilst it retains its original size and greenish colour near the anode. The bright kathode spot gives the subordinate series as strong lines. Rubidium and caesium resemble potassium, but they give their colours to a portion of the flame near the kathode.

Calcium, strontium, and barium give brilliant colours to the flame near the kathode when beads of their chlorides

are used, and their spectra at the kathode resemble their oxyhydrogen flame spectra, whilst the spectra of the coloured flames are more like those of their Bunsen flame spectra.

Experiments have been made with metallic electrodes of magnesium, aluminium, zinc, tin, and lead. These metals give bright spots on both electrodes and there are differences between the spectra of these. The spectra of the anode spots on magnesium and aluminium contain the "oxide bands" of the metals, but these bands have not been observed in the kathode spots. The writer is continuing the study of this subject in the hope of gaining further knowledge on the constitution of electric sparks and the origin of the spectra.

(NOTE.—Since the above paper was written it has been found by examination of the sparks in a rotating mirror that the coloured flames actually shoot out from the kathode. There was practically no colour given to the spark by the matter thus expelled in an atmosphere of hydrogen; colours were obtained in some instances in nitrogen, but the experiments are not yet concluded. The spectra of the bright spots on the kathodes are always brighter in hydrogen than in air or oxygen, and they are usually brighter under pressures somewhat below the ordinary atmospheric pressure. Zinc and cadmium were reduced from electrodes of their oxides when these were in hydrogen. Their vapours were shot off from the electrode and films of the metals condensed in the form of rings on the tube and on pieces of perforated mica placed in the path of the spark).—*Proceedings of the Cambridge Philosophical Society*, xii., Part 5.

CHEMICAL EQUILIBRIUM BETWEEN FERRO- AND FERRICYANIDE OF POTASSIUM IN THE PRESENCE OF ALKALIS.

By MAURICE PRUD'HOMME.

A SOLUTION of ferricyanide of potassium is partially transformed into ferrocyanide when it is submitted to a prolonged boiling with potash. The transformation is integral if we cause the intervention of a reducing body, such as glucose, indigo, &c., which will be oxidised by the oxygen set free.

This property was made use of by Mercer to produce white prints on an indigo blue background. I have examined separately the influence of the quantities of red prussiate, caustic soda, and yellow prussiate on the times necessary for the oxidation or the decolouration of indigo, and have obtained the following results:—

1. The speed of the oxidation of indigo by a mixture of the red prussiate and caustic soda is as nearly as possible proportional to the quantities of the red prussiate and caustic soda used:—

$$V = cR + c', \quad V_1 = c_1S + c'_1.$$

2. The speed of the oxidation of indigo by a mixture of red prussiate, caustic soda, and yellow prussiate is as nearly as possible inversely proportional to the amounts of yellow prussiate when the latter alone is varied.

The fact that the transformation of the red prussiate into the yellow prussiate is not complete, except in the presence of a reducing agent, can be explained by the existence of a state of chemical equilibrium between the elements present:— $\text{Fe}_2\text{C}_6\text{H}_6\text{K}_6 + 2\text{KOH} \rightleftharpoons 2\text{FeC}_6\text{H}_5\text{K}_4 + \text{H}_2\text{O}_2$.

The variations undergone by the speed of the oxidation of indigo, through the presence of the yellow prussiate, corresponds to a phenomenon analogous to that of the etherification of the alcohols, where the addition of an excess of alcohol, acid, ether, or water changes the limit of the chemical equilibrium or of the etherification.

In the equilibrium equation given above, peroxide of

hydrogen is observed; this signifies nothing more than that it is actually formed during the reaction. Nevertheless, it seemed important to examine its action on the yellow and red prussiates, as well as on the indigo itself.

Action of Peroxide of Hydrogen on the Prussiates and on Indigo.

1. Neutral peroxide of hydrogen, added in suitable proportion to a solution of yellow prussiate, transforms this latter into red prussiate with the liberation of potash. The solution turns an alcoholic solution of phenolphthalein strongly red, turns red litmus-paper blue, and decolourises indigo blue, but only very slowly, because the amount of caustic alkali present is a minimal quantity.

2. A solution of red prussiate and caustic soda treated with an excess of peroxide of hydrogen changes colour immediately, and is then decolourised, and at the same time it loses all oxidising action on the indigo. The colourless solution, left to itself or heated, gives off oxygen and re-assumes a pale yellow colour; the yellow prussiate is re-formed, and this crystallises if the solution is sufficiently concentrated. There should be produced a colourless combination between the red prussiate and the peroxide of sodium, resulting from the action of the peroxide of hydrogen on the soda. This combination is finally resolved into oxygen and yellow prussiate.

These two inverse reactions (1 and 2) easily explain the state of equilibrium in which an alkaline solution of red prussiate must remain so long as we do not bring in the action of a reducing agent.

3. Peroxide of hydrogen, at about 12 volumes, in the presence of dilute sulphuric acid, slowly decolourised indigo blue. At the temperature of 70° it requires about fifteen hours to decolourise a sample of cotton-cloth containing 0.5 grm. of indigotine to the square metre. Fresh peroxide of hydrogen must be added when the evolution of of gas becomes too slow, or even the whole solution may be renewed.

4. In the presence of an alkali, such as soda, the decolouration of indigo by peroxide of hydrogen is much more rapid, and takes place in two and a-half hours at 70° , or five times as quickly as in acid solution. In the cold it takes almost a week to produce decolouration, or sixty times as long as at 70° .—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 20.

DETERMINATION OF THE CARBONATE OF SODIUM NECESSARY TO PRECIPITATE THE LIME AND MAGNESIA FOR THE CHEMICAL PURIFICATION OF WATER.

By LEO VIGNON.

THE method I have described already (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 559) consists of measuring directly the amount of carbonate of sodium necessary for the chemical purification of water.

In the presence of alcohol and phenolphthalein, the chlorides and sulphates of calcium and magnesium are first transformed into salts of sodium, then the excess of carbonate of sodium is shown by the red colouration of the phenolphthalein; the addition of alcohol accelerates the reaction.

Having applied this method to a very large number of waters, I have accumulated a series of observations which have enabled me to improve it, and to adapt it in the best possible manner to the different cases which occur in practice.

I will sum up the observations made:—

1. The estimation of the carbonate of sodium effected by the method indicated corresponds to the amount of this salt reacting under the conditions of dilution, time, and temperature of the experiment. Let A be this quantity.

2. We can estimate the carbonate of sodium necessary for the complete transformation of the chlorides and sulphates by boiling a known volume of the water under examination in a platinum or nickel crucible with a known amount, in excess, of a titrated solution of carbonate of sodium for thirty minutes. The titration of the mixture after the reaction shows by difference the amount of carbonate of sodium used in the reaction. This amount, B, corresponds with the dilution and temperature (boiling-point), and also with the fact that the carbonate of sodium is in excess. In practice we always find B greater than A; this is explained easily by the fact that in the second case the reaction at boiling-point has been more complete than at the ordinary temperature.

3. By using the colorimetric method, to estimate the excess of carbonate of sodium by phenolphthalein, we observe that after being exposed for some time to light or heat the violet colouration of the liquor disappears gradually. Thus light and heat act on this colouration, and may cause errors if the operation is prolonged.

The action of light and heat is not very strong, however, during the time of the experiment, and the amount of carbonate of sodium found (A) is truly that which corresponds to the reaction of this salt on the chlorides and sulphates of lime and magnesium at the ordinary temperature; but if we leave the substances in contact for twenty-four hours at the ordinary temperature, we find that A increases. Its value approaches that of B by amounts varying for the same time, according to the water examined. By prolonging the contact for several days, and by varying the conditions (ordinary temperature—temperature of 50°; light—darkness), A reaches and surpasses B when the influence of heat or light manifests itself, while A becomes and remains equal to B without surpassing it, after a lapse of time, variable according to the kind of water analysed, when kept at the ordinary temperature and in the dark.

4. If we consider the quantity B, corresponding to the carbonate of sodium, having reacted on the water at boiling-point, in the presence of an excess of this salt, we may ask whether this amount, B, would all enter into the reaction if the exact amount were used without any excess. The last portions of the carbonate of sodium, being very dilute in the mixture, might not enter into the reaction.

Experiment shows that by treating a known water with the amount B, the water remains alkaline, the last portions of the carbonate of sodium not having reacted.

In an experiment the amount B was equal to 280 grms. per cubic metre of water; after boiling for thirty minutes in a nickel crucible, 10 grms. of free carbonate of sodium, remained per cubic metre, or 1/100,000th.

In a second experiment on another water, B being equal to 102 grms. per cubic metre, there remained, after boiling for thirty minutes in the nickel crucible as a result of several trials, from 9 to 20 grms. of free carbonate of sodium per cubic metre of water, or from 9 to 20 millionths.

At each temperature maintained during a given time, we find for each water that a certain quantity, Q, of carbonate of sodium comprised between A (the carbonate of sodium reacting at the ordinary temperature) and B (the carbonate of sodium reacting at boiling temperature in the presence of an excess of carbonate of sodium) should be used in practice. This quantity is that which reacts almost entirely on the chlorides and sulphates, and leaves only a very slight trace of free carbonate of sodium in the water. Practically the free carbonate of sodium should not exceed 10 grms. per cubic metre, or 10 millionths.

The determination of this quantity comprised between A and B should be effected while considering the end aimed at in the chemical purification of the water, and by realising the practical conditions of time and temperature of the operation. If the water is treated at the ordinary temperature, Q will be very close to A; if, on the contrary, the water is for use in boilers, the quantity Q, will be much closer to B.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 3.

FURTHER EXPERIMENTS ON THE PRODUCTION OF HELIUM FROM RADIUM.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.,
and
FREDERICK SODDY, M.A.

THE research, of which a preliminary account has already been given in the *Proc. Roy. Soc.*, vol. lxxii., pp. 206 and 208, has been continued with the view of ascertaining the volume of emanation produced in a given time from a known weight of radium in the form of bromide, and also the quantity of helium resulting from the spontaneous change of the emanation.

Owing to the minute quantity of material at our disposal, the research has been a somewhat tedious one; but we have succeeded in obtaining fairly concordant measures of the volume of both emanation and helium. The present paper gives a description of the apparatus employed, the methods of experiment, and the quantitative relation between radium and its products.

The inactive nature of the emanation from thorium was the subject of an investigation by Rutherford and Soddy (*Nat. Mag.*, 1902, 16, vol. iv., p. 581). They concluded "that it is a chemically inert gas analogous in nature to the members of the argon family." And they continue: "The speculation naturally arises whether the presence of helium in minerals and its invariable association with uranium and thorium may not be connected with their radio-activity." The discovery was thus the subject of prediction. It followed an attempt to obtain the spectrum of the emanation. Thinking that the spectrum, if brilliant, might be observed by mixing the emanation with a gas of simple spectrum, the first experiments were made by mixing it with helium; but it soon became evident that the helium spectrum overpowered that of the emanation to such an extent as to mask it entirely. And experiments on the removal of gases not belonging to the argon group from the emanation convinced us that its quantity was so small as to require special contrivances in order to deal with it. All apparatus, consequently, was constructed on a minute scale of capillary tubing, less than half a millimetre in diameter. Approximate measurements of the scale of the apparatus in centimetres are given in the sketches.

Fig. 1 gives a sketch of the first apparatus, which was soon abandoned; suffice it to say that an attempt was made to accumulate the emanation in A, which contained a solution of several grms. of impure chloride, obtained from very impure carbonate, and to examine its spectrum in the U-tube B, made of capillary tubing, with electrodes of platinum as shown. The spectrum was that of carbon monoxide and dioxide.

Experiment 1.—A brief description of this experiment has already been given (*Proc. Roy. Soc.*, lxxii., 206). Twenty milligrams of radium bromide was dissolved by admitting water boiled *in vacuo* to the crystals in the bulb A (Fig. 1), which had previously been freed from air with the pump. The bromide, as a letter from the seller informed us, had been prepared in the solid state about two and a-half months. The evolved electrolytic gas containing the emanation was collected through the pump and introduced into the apparatus, of which a sketch is given in Fig. 2. Before this was done, the whole apparatus had been exhausted, and washed out with oxygen several times, admitted through the gas-burette. The emanation, too, was collected in a tube which had been used for oxygen, the object being to keep nitrogen out of the tubes, and so to avoid its spectrum, which is difficult to remove.

The gas, of which there was about half a c.c., was admitted into the gas-burette through the inverted syphon A; the stopcock being reversed, it was passed slowly into the tube B, which contained a spiral of thin, partially oxidised copper wire, and which had previously been exhausted; during the introduction of the gas the copper

* A Paper read before the Royal Society, April, 1914.

spiral was kept red-hot by a current. The water produced was absorbed in the tube c, which contained phosphorus pentoxide. Mercury was then admitted into b and c, so as to displace the gas through the stopcock d, which was then shut. The vacuum tube r had been previously glowed out until phosphorescent. This vacuum tube is represented in natural size in Fig. 3; its capacity was about one-third of that of the U-tube and accessory tubing. The spectrum of carbon dioxide was alone seen. With a jar and spark-gap interposed, on comparing the spectrum with the jar discharge in a similar tube containing carbon dioxide, a yellow line was visible in the gas from radium, and also a bright blue line, absent in the spectrum of the pure dioxide. The spectrum of helium was then thrown in through a comparison prism, when no doubt remained that the yellow line was actually D_3 . By cooling the U-tube, the emanation and dioxide were condensed, and the helium spectrum increased greatly in brilliancy. After half-an-hour the tube was sealed off. The position of the D_3 line was con-

approximate wave-length 6145 and 5675, the former faint but distinct, the latter moderately bright. The vacuum-tube did not glow visibly in the dark, showing that the emanation had been almost completely removed. The U-tube was next placed in communication with the pump, still surrounded with liquid air, but no gas could be extracted; now the U-tube had probably two or three times the capacity of the vacuum-tube; and at the low temperature of liquid air, almost twenty times the quantity of helium must have remained in it. It shone brilliantly in the dark. The passage to the pump was then closed, and the liquid air removed. On again establishing communication, a brilliant phenomenon was observed in the dark; the glowing emanation passed through the capillary somewhat slowly, rushed along the wider connecting tubing, was delayed in passing through the tightly packed phosphorus pentoxide, and finally filled the barrel of the Töpler pump. On raising the reservoir, the gas grew more luminous as its volume was decreased, and on

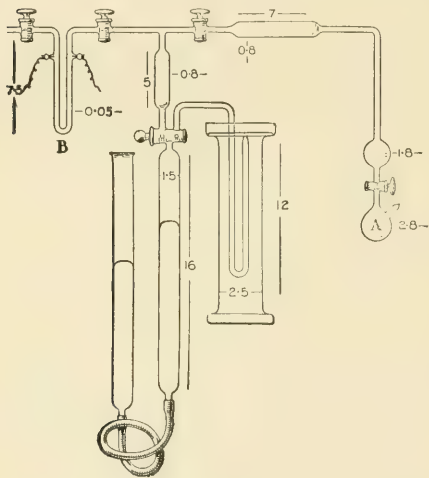


FIG. 1.

firmed to within one-tenth of the distance between the two sodium lines, D_1 and D_2 .

Experiment 2.—A second apparatus similar to the last was made of entirely fresh glass, so as to exclude any possibility of contamination with helium; and the observation was repeated with 31.8 milligrams of radium bromide, kindly lent by Prof. Rutherford, which had been kept in the solid state at least three months. The apparatus was slightly modified, as shown in the dotted lines in Fig. 2, so as to avoid taking the gas through the pump. As before, the whole apparatus was washed out with oxygen, and the copper spiral was glowed in oxygen, so as to oxidise it superficially, and so render it able to deal with the excess of hydrogen, as well as with the constituents of the water which had been decomposed. After the gas had been admitted by opening the stopcocks G and H, the copper spiral was kept glowing for three-quarters of an hour. The U-tube was then cooled with liquid air, and tap d was opened. D_3 was seen. Mercury was admitted to the tubes b and c, and the vacuum-tube was sealed off. It now showed all the visible helium spectrum except the faint least-refrangible red, as well as the yellows, green, and violet of mercury. Two unidentified lines were also measured, of

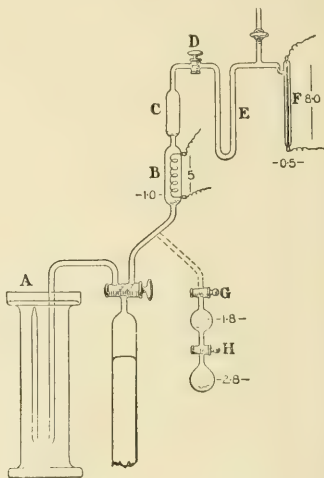


FIG. 2.

lowering it, the glowing gas appeared to lie on the surface of the mercury for a fraction of a second, falling with the falling mercury; but it soon spread through the whole barrel by diffusion.

The bubble of gas pumped out was treated with a drop of caustic potash, when a considerable fraction was absorbed. By next day the volume of the bubble had increased.

Inasmuch as all samples of emanation showed the spectrum of carbon dioxide, the presence of which was believed to be due to the oxidation of the tap-grease, an apparatus was constructed in which the use of taps was, as much as possible, avoided. All the emanation from about 60 milligrams of radium bromide was introduced into the burette A, the only gas present being oxygen. From the burette it passed through the bulb B, which contained concentrated potash solution; it then passed through c, which was charged with solid potash and was deprived of moisture by contact with phosphorus pentoxide in d. The level of the mercury in the trap was at e, so that the emanation reached the spiral G, cooled with liquid air; the whole of the emanation was washed into the spiral by admission of a little pure oxygen from A; on exhaustion with

the pump the gas was not luminous, showing that the emanation had been almost completely retained in the spiral. Mercury was then allowed to rise in the trap until the bulb F was filled; the connection to the pump was then sealed at H and the spiral allowed to warm up. The emanation in the vacuum tube showed a bright green spectrum, but on filling the spiral with mercury and sealing off the vacuum tube, the spectrum of carbon dioxide became visible; D_3 was not seen.

Next day this line was seen, but very feeble; its strength increased from day to day, and in five days the yellow, green, and two blues were visible as well as the violet; their identity was proved by means of a comparison spectrum.

Subsequent experiments were made in which the heated spiral of copper was replaced by a tube containing a fragment of phosphorus; the emanation was washed out of

19.48 c.c.; oxygen, 10.37 c.c.; nitrogen, 1.02 c.c. = 30.87 c.c.

The nitrogen was manifestly derived from leakage; after deducting one-fourth of its volume of oxygen, the remaining gas has practically the composition of electrolytic gas. The rate of accumulation is about $\frac{1}{3}$ c.c. a day.

The object of the experiment, of which an account will now be given, was to form an estimate of the amount of helium produced by comparing the intensity of its spectrum with that of a known quantity of helium at a known pressure.

Experiment 3.—This gas was exploded and left a residue of nitrogen; it was then mixed with a large excess of oxygen, and sparked in presence of caustic soda for some hours to remove nitrogen. The oxygen was next withdrawn by means of phosphorus, and the minute bubble

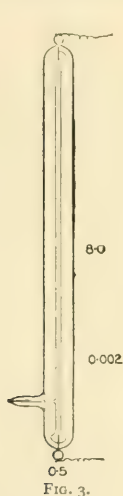


FIG. 3.

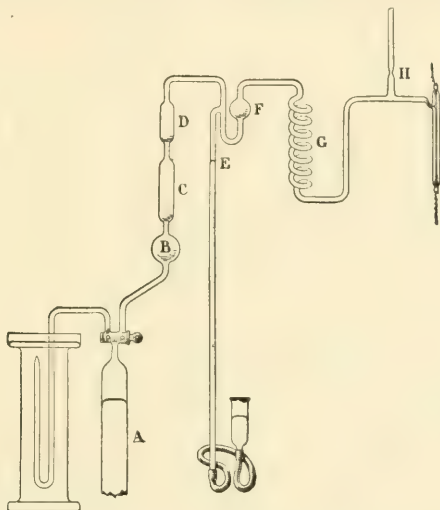


FIG. 4.

the condensing tube by a few bubbles of oxygen. The bulb of potash solution was retained, but the solid potash was replaced by solid barium hydroxide. This plan was not so effective in removing carbon dioxide, yet on keeping the tube for three days, and condensing the carbon dioxide with liquid air, D_3 was easily visible, although weakened by the spectrum of carbon monoxide.

On two subsequent occasions the gases evolved from both solutions of radium bromide were mixed after four days' accumulation, which amounted to about 2.5 c.c. in each case, and were examined in a similar way. In this case the non-condensable gases alone were examined, the emanation being retained. Whereas with the emanation almost the whole can be introduced into the vacuum tube, with permanent gases only about one-twentieth part is available for the purpose of the spectrum. The D_3 line of helium could not be detected.

The vacuum now intervened, and the bulbs containing the dissolved radium bromide were connected with a mercury reservoir and with a gauge, so that the pressure should not rise and burst the bulbs. The gas accumulated during sixty days; its composition was: Hydrogen,

left was mixed with a bubble of oxygen, in order to wash it into the apparatus to which the vacuum tube was sealed. As already described, this apparatus did not differ from that shown in Fig. 2, except for the fact that the tube containing the copper spiral was replaced by one containing a fragment of phosphorus, in order to withdraw the oxygen. The phosphorus was warmed and withdrew the oxygen. The gas was then forced by means of mercury through a cooled U-tube, and a portion reached the vacuum tube. On passing a current for an instant, the D_3 line was plainly seen, but nitrogen was also present in small amount. The tube was then sealed off.

The volume of the spectrum tube, including the U-tube, had been previously estimated by filling it twenty times with air and pumping out each time; from this measurement the total volume was found to be 0.310 c.c., and after the U-tube had been sealed off, the same process was repeated with the U-tube and connections, minus the spectrum tube. The volume of the spectrum tube was thus found to be 0.165 c.c.

An exactly similar spectrum tube made of the same glass and having the same length was attached to a bulb

tube, from which it could be cut off by turning a stopcock; the bulb tube in its turn could be cut off from the pump by a stopcock. The capacity of the spectrum tube as well as of the bulb tube was known. A known amount of helium was introduced into the bulb tube and the spectrum tube by means of an inverted syphon furnished with two stopcocks; the volume between the stopcocks was 0.0268 c.c. As the volume of the spectrum tube and connections was 1.68 c.c., and that of the bulb was 1.25 c.c., when the gas contained in the spectrum tube was allowed to expand into the evacuated bulb tube, its volume was reduced in the ratio $1.68 : 1.25 + 1.68$, or 0.57. The spectrum tube containing the fraction of the helium from 60 days' accumulation was placed in series with that containing helium, so that the same current traversed both, and their spectra were compared as regards luminosity of the D_3 line. It was necessary to divide the contents of the helium tube seven times before the D_3 line could be regarded as of comparable intensity in both spectrum tubes. Multiplying this ratio by the volume of the helium admitted at atmospheric pressure into the apparatus, the volume remaining in the apparatus after rarefaction is given:—

$$(0.57)^7 \times 0.0268 = 0.000517 \text{ c.c.}$$

Now the volume of the helium tube and connections was by chance practically ten times that of the spectrum tube alone (1.65 and 0.165), hence the spectrum tube contained 0.000052 c.c., or 0.052 cub. m.m. The total quantity obtained was twice this amount, or 0.1 cub. m.m.

As 1 litre of helium weighs 0.18 grm., for its density is twice that of hydrogen, 0.1 cub. m.m. weighs 0.000018 m.grm. This amount is the product of 50 m.grms. of radium bromide in 60 days; hence, 1 grm. of the bromide should give in a year 0.0022 m.grm. It should be mentioned that the spectrum of argon was present, and it may have seriously interfered with this estimation. The helium, too, may have penetrated and been retained in the glass.

Experiment 4.—It appeared feasible to attempt to measure the actual volume of the emanation in a fine capillary tube. Thinking that any bought capillary tube would be too wide, we drew a very narrow one, which had an electrode sealed into its end. It turned out, however, to be very irregular, and the results as regards volume are not very trustworthy. A is the capillary tube, with a platinum electrode of very fine wire sealed into its upper end; the mixed hydrogen and oxygen containing the emanation were introduced into the explosion burette F through the inverted syphon E; some moist caustic potash had been melted in the top of the burette, so as to remove from the gases any possible carbon dioxide which might have been produced by the flame causing any organic dust in the burette to burn. After the gases had been exploded, the excess of hydrogen, together with the emanation, was allowed to stand for some time in contact with the caustic potash. The upper part of the apparatus having been completely evacuated, the connection with the pump was closed, and the tube leading to the reservoir of the burette was clipped; on making communication by turning the tap of the burette, the hydrogen and the emanation entered the apparatus. Liquid air was then poured into the tube C, so as to cool the bulb B, where the emanation condensed. After raising and lowering reservoir of the burette several times, in order to convey the emanation into the bulb B, the tap of the burette was closed, and that leading to the pump opened. Again opening cautiously the tap of the burette, the mercury was allowed to rise, passing through the tube D containing phosphorus pentoxide as far as G; the evacuation was then completed until not a trace of a bubble passed through the pump. The tap leading to the pump was closed, and that of the burette opened, until the mercury had risen to near the bulb B. On darkening the room the bulb B was brilliantly luminous; indeed, it was possible to read a watch by its light. The liquid air was allowed to evaporate away, and the reservoir of the burette

lowered and its tap opened; by gently raising the reservoir the emanation was all collected in the capillary tube A. The volume of the emanation was read from day to day by help of a reading telescope. It contracted regularly; the tube was coloured deep purple after some days, and this made reading difficult, but by a brilliant illumination behind the rise of the mercury could be followed. No attempt was made to pass a discharge for twenty-eight days; after that lapse of time the emanation had contracted to a volume occupying only 0.1 of a m.m. of the capillary tube at a pressure of about 50 m.m., yet it maintained its brilliancy till the very last; only the length of tube illuminated grew shorter and shorter. On freezing out the mercury vapour by cooling the bulb B with liquid air, the

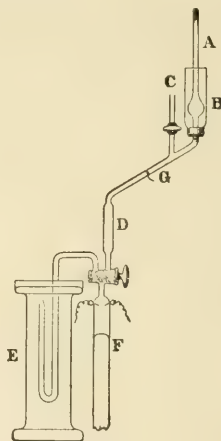


FIG. 5.

helium spectrum was visible, and at the same time the effect of passing the discharge was to reproduce gas in the capillary tube.

After the conclusion of the experiment, the tip of the tube was cut off immediately below the platinum wire, and the capillary depression was measured at different levels. The capillary tube was then cut off, and the volume determined by weighing with mercury; it was then calibrated by a shifting thread of mercury, under a reading microscope. The final results were:—

Time.	Volume.
Start	0.124 cub. m.m.
One day	0.027 "
Three days	0.011 "
Four days	0.0095 "
Six days	0.0063 "
Seven days	0.0050 "
Nine days	0.0041 "
Eleven days	0.0020 "
Twelve days	0.0011 "
Four weeks	0.0004 "

The comparatively large volume at the start is very remarkable; we can only record it, it may possibly have been due to the mercury sticking in the capillary tube, which was narrower below.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 5th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

(Concluded from p. 247).

79. "The Resin Acids of the Coniferae. Part I. The Constitution of Abietic Acid." By THOMAS HILL EASTERFIELD and GEORGE BAGLEY.

The resin acids of the *Coniferae* as a class have the following points in common:—(1) They readily become superheated, and then set to a resin or glass, which crystallises if fused and maintained for some time at a temperature slightly above the initial melting-point; (2) they nitrate without difficulty in glacial acetic acid solution; (3) in a fused state, they readily absorb oxygen from the air; (4) their esterification velocity is extremely low; (5) with hydriodic acid, they yield hydrocarbons of nearly the same composition as the diterpenes, with which they have erroneously been regarded as identical.

Colophony, on distillation under diminished pressure or in superheated steam, yields a product which gives analytical results agreeing accurately with those required for abietic acid (m. p. 100–105°).

By the slow distillation of abietic acid, even under reduced pressure, a hydrocarbon, $C_{18}H_{28}$, is produced, which is undoubtedly the "colophene" obtained by Deville on distilling colophony, but is not the "colophene" which the same author produced by polymerising turpentine by means of sulphuric acid. In order to avoid ambiguity, the name "abietene" is proposed for the compound derived from abietic acid.

Kramer and Spilker, by distilling colophony under pressure, obtained a hydrocarbon to which they assigned the formula $C_{18}H_{28}$, regarding it as being derived from abietic acid by the loss of carbon dioxide.

Abietene, $C_{18}H_{28}$, boils at 199–200° (13 m.m.), 247–250° (82 m.m.), 340–345° (760 m.m.), has a sp. gr. 0.973 at 19/19°, and n_D^{20} 1.537 at 20°; it is thus identical with the "diterbenthyl" ($C_{20}H_{30}$) which Renard (*Comptes Rendus*, 1887, cv., 865) isolated from resin oil.

Abietene is produced when abietic acid is heated with fuming hydriodic acid at 200°; the gases formed at the same time have been analysed, and were found to consist of 90 per cent of carbon monoxide and dioxide approximately in the ratio $9CO : 1CO_2$, the volume of oxides of carbon formed after two hours' heating being 80 per cent of that required for the elimination of one carboxyl group from abietic acid.

Abietene, when distilled with one-third of its weight of sulphur, yields a small quantity of retene (m. p. 99°), but with twice this proportion of sulphur an isomeric hydrocarbon is obtained melting at 86°; at the same time, a hydrocarbon boiling at 330–360° (30 m.m.) is produced, which is still under examination. If the distillation with sulphur is conducted under reduced pressure, retene is the principal product. These two hydrocarbons are also formed by distilling Merck's "retene puriss." with one fifth of its weight of sulphur.

The foregoing observations support the view that hydrogenated retenes are probably normal constituents of resin oil (*Ber.*, 1899, xxii., 3368; 1903, xxxvi., 647), and that resin oil is undoubtedly a hydrogenated retene.

This conclusion is further strengthened by the observation that abietene, when reduced with hydriodic acid and excess of phosphorus at 240°, takes up two atoms of hydrogen and yields a hydrocarbon, dihydroabietene, which appears to be identical with the dodecahydroretene obtained by Liebermann and Spiegel (*Ber.*, 1889, xxii., 779) by reducing retene under similar circumstances.

The above observations lead to the conclusion that abietic acid is decahydroretene-carboxylic acid, but the

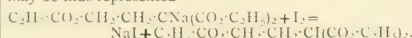
accepted formula for retene would not account for its low esterification velocity. There is, however, no experimental evidence for the assumed para-position of the methyl and isopropyl groups in retene. That these groups are really in the meta-position in abietic acid and in retene is rendered probable by the observation of Kolbe (*Ber.*, 1880, xiii., 888) that resin spirit is rich in *m*-cymene, but contains only small quantities of ordinary cymene.

80. "The Additive Products of Benzylideneaniline with Ethyl Acetoacetate and Ethyl Methylacetoacetate." By FRANCIS ERNEST FRANCIS and MISS MILDRED TAYLOR.

It was shown that the additive product of benzylideneaniline and ethyl methylacetoacetate exists in one form only, being unaffected in solution by traces of either piperidine or sodium ethoxide. This confirms Schiff's view of the constitution of such substances. The various data in connection with the additive products from ethyl acetoacetate and benzylideneaniline were indicated, and Morrell and Bellars' work on the subject was criticised.

81. "Studies on Ethyl Carboxyglutarate. Part I. Action of Halogens on Ethyl Sodiocarboxyglutarate." By OSTWALD SILBERRAD and THOMAS HILL EASTERFIELD.

When halogens were allowed to act on ethyl sodiocarboxyglutarate, no condensation occurred, but instead of ethyl carboxyglutarate the haloal derivatives of the original ethyl carboxyglutarate were formed. The reaction may be thus represented—



The products proved to be identical with the compounds subsequently obtained by the direct halogenation of ethyl carboxyglutarate.

82. "Studies on Optically Active Carbimides." Part I. By ALLEN NEVILLE and ROBERT HOWSON PICKARD.

The authors have investigated (i.) the preparation of some optically active carbimides, (ii.) the use of such compounds for the resolution of synthetical alcohols and amines containing asymmetric carbon atoms, (iii.) the measurement of the velocity of reaction between such compounds and various alcohols and amines with the object of contrasting the influence of (1) the constitution of the alcohols and amines, (2) the temperature, (3) the solvents, and (4) various catalytic agents on the velocity of such reactions.

The compounds described were:—Boranylcarbimide (compare Forster and Attwell, *Proc.*, vol. xx., p. 91), ethyl boranylcarbimide and diboranylcarbimide, 1-menthylcarbimide, methyl ethyl, and propyl 1-menthylcarbimide, and di-1-menthylcarbimide.

83. "The Comparison of the Rotation Values of Methyl, Ethyl, and *n*-Propyl Tartrates at Different Temperatures." By THOMAS STEWART PATTERSON.

Methyl tartrate was first shown to be capable of existence in a solid form melting at 61.5°.

Data for the variation of rotation with change of temperature of methyl, ethyl, and propyl tartrates were given. Comparisons of the rotation values of these substances at identical temperatures were shown to be of little value, especially at low temperatures. Since, however, the rotation of methyl tartrate vanishes at 0°, that of ethyl tartrate probably at –34°, and that of propyl tartrate probably at –60°, it may be assumed that the three substances are in corresponding optical conditions at these temperatures, and, in general, methyl tartrate at T° , ethyl tartrate at $(T - 34)^\circ$, and propyl tartrate at $(T - 60)^\circ$ will also be in corresponding conditions as regard rotation. It is shown that comparisons of rotation effected at corresponding temperatures are much more satisfactory than those obtained for identical temperatures, and that if the rotations are taken at corresponding temperatures, the increment of $2CH_2$ in passing from methyl to ethyl tartrate rather more than doubles the rotation, whilst the next increment of $2CH_2$ in passing to propyl tartrate increases the rotation to 1.41 times that of ethyl tartrate. The

rotation of propyl tartrate is therefore almost three times that of methyl tartrate. These results hold within wide limits of temperature.

84. "Note on the Action of Hydrogen Sulphide on Formaldehyde and Acetaldehyde Solutions." By JULIEN DRUGMAN and WILLIAM ERNEST STOCKINGS.

Although the conditions under which various thio-derivatives are formed when hydrogen sulphide reacts with aqueous solutions of formaldehyde and acetaldehyde respectively have been thoroughly investigated by Hofmann (*Ber.*, 1868, i., 176; 1869, ii., 152; 1870, iii., 584), Pirner (*Ber.*, 1871, iv., 257), Klinger (*Ber.*, 1876, ix., 1894; 1877, x., 1879; 1878, xi., 1023), Baumann and Fromm (*Ber.*, 1889, xxii., 2600; 1890, xxiii., 69; 1891, xxiv., 1434, 1457), and others, it is not generally known that, provided hydrochloric acid or other strong mineral acid is absent, the reaction affords a sure means of detecting formaldehyde, even in the presence of acetaldehyde or other higher fatty aldehydes.

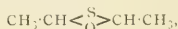
1. When a dilute aqueous solution of formaldehyde is saturated with hydrogen sulphide in the absence of hydrochloric acid, and the test-tube set aside in a warm place (30°–50°), no visible change occurs for about three or four hours, but afterwards a white, amorphous, flocculent precipitate is gradually deposited. This substance, when dried in a desiccator over sulphuric acid, melts, with decomposition, between 85° and 110°.

This characteristic thio derivative is precipitated from formaldehyde solution by hydrogen sulphide even in the presence of acetaldehyde, methyl, and ethyl alcohols, acetone, or acetic acid; the melting-point of the product formed in presence of acetone or acetic acid is fairly definite, namely, 98°–103°, and sometimes quite sharp at 98°. According to Baumann (*loc. cit.*), the compound has the composition $3(\text{CH}_2\text{S})\cdot\text{CH}_2\text{O}$; it is distinguished from the odourless, crystalline trithioformaldehyde, $(\text{CH}_2\text{S})_3$, both by its lower melting-point and strong odour. The presence of even 0.1 per cent of formaldehyde in aqueous solution may be easily detected by means of this reaction.

2. The crystalline trithioformaldehyde, $(\text{CH}_2\text{S})_3$, first prepared by Girard by the reduction of carbon disulphide by means of nascent hydrogen (*Comptes Rendus*, 1870, lxx., 623), and afterwards fully investigated by Hofmann (*loc. cit.*), results when hydrogen sulphide acts on a solution of formaldehyde previously strongly acidified with hydrochloric acid. The crude product melts indefinitely between 180° and 205°, but it crystallises from hot acetone in white needles which melt at 216°.

3. When a solution of acetaldehyde is saturated with hydrogen sulphide in the absence of hydrochloric acid or other strong mineral acid, and the test-tube set aside in a warm place, the liquid soon assumes a milky appearance, owing to the separation of minute, oily particles, which gradually collect in drops on the bottom and sides of the test-tube, leaving the rest of the liquid perfectly clear and translucent. No solid product is ever obtained under these conditions, a circumstance which at once differentiates the behaviour of acetaldehyde from that of formaldehyde.

4. Several distinct crystalline thio-derivatives can be obtained by the action of hydrogen sulphide on aqueous or alcoholic solutions of acetaldehyde previously acidified with hydrochloric acid. Among these may be mentioned the volatile bimolecular compound,—



which melts at 61°, and the α -, β -, and γ -trithioacetaldehydes, $(\text{C}_2\text{H}_4\text{S})_3$, which melt at 101°, 125°–126°, and 76° respectively. The character of the products and the relative proportions in which they are formed depend entirely on the experimental conditions. When, however, a dilute (1 to 20 per cent) aqueous solution of acetaldehyde, acidified with about one-fifth of its volume of strong hydrochloric acid, is saturated with hydrogen sulphide, and the test-tube set aside in a beaker over a water-bath kept at

50°–60°, a very characteristic and striking phenomenon is observed. At the outset, the liquid assumes the milky appearance described under (3), then gradually becomes clear, and finally, after some hours, a volatile thio-compound sublimes on to the cooler portions of the tube in the form of long, glistening needles, which, after crystallisation from acetone or dilute alcohol, melt at 75°–78°. The sublimate is not, however, formed if the original solution contains formaldehyde as well as acetaldehyde. In this case, the mixed thio-compounds separate together from the liquid as a crystalline precipitate. Moreover, if the original solution contains a volatile solvent, such as acetone or alcohol, the sublimate will only appear after the solvent in question has nearly all evaporated.

5. Aqueous solutions of propaldehyde or isobutaldehyde saturated with hydrogen sulphide, without any addition of hydrochloric acid and set aside in a warm place, exhibit a similar behaviour to that of acetaldehyde solutions under the same conditions. The oily thio-compounds obtained soon fall to the bottom of the test-tube, leaving the supernatant liquid quite clear. The presence of hydrochloric acid does not materially alter the character of the appearances observed, except in the case of isobutaldehyde, when, after a very long time, a slight crystalline sublimate may be formed.

85. "The Viscosity of Liquid Mixtures." By ALBERT ERNEST DUNSTAN.

The following conclusions were drawn from the author's investigation on the viscosity of liquid mixtures:—

1. Aqueous solutions give abnormal results. This is true for all known cases, which, however, are always solutions of two associated liquids, as, for example, alcohol and water.

2. Whenever chemical affinity is existent to any marked extent in the two liquids of a mixture, abnormal results occur. In many such cases, definite complexes have been isolated.

3. Whenever marked abnormalities present themselves, it is noted that they do so near points of definite molecular composition, but these points of abnormality are not constant, and shift with change of temperature. At a sufficiently high temperature, they would probably vanish, as then no formation of complexes would be possible.

4. When points of minima are obtained in the viscosity curve, it is difficult to say whether association or dissociation is proceeding. It certainly seems due to some change in molecular aggregation.

5. Substances containing the hydroxyl group (and associated) have a higher viscosity, as a rule, than monomolecular substances. Hence the rise of viscosity in the case of alcohol—water is probably due to the formation of complexes.

A further examination of hydroxylic substances is in progress.

86. "The Conversion of Isopropyl Alcohol into Isopropyl Ether by Sulphuric Acid." By FRANK SOUTHERDEN.

In the course of some experiments on etherification by the agency of small quantities of sulphuric acid at high temperatures, it has been found possible to prepare isopropyl ether. The yield is very poor, and therefore without improved conditions the method cannot be said to compete with that involving the use of alkyl iodide (Erlenmeyer, *Annalen*, 1863, cxxvi., 305), but it is interesting as an example of the production of a secondary ether from its alcohol.

Previous observers have obtained only propylene in this reaction. When, however, 5 c.c. of H_2SO_4 were employed for 100 c.c. of isopropyl alcohol (b. p. 81°–83°), and the mixture heated for six to twelve hours at 150°–160°, the ether was formed along with propylene. After removal of the unchanged alcohol by prolonged treatment with sodium, the whole distilled at 70°–70.5° (uncorr.). Zander (*Annalen*, 1882, ccxiv., 164) gives 68°–69° as the boiling-point of the ether. The isopropyl ether has an intense odour resembling peppermint; bromine in carbon tetrachloride

solution is not decolorised by it. Two vapour density determinations obtained by Victor Meyer's method gave 51.3 and 51.4, whereas the calculated value for $(C_2H_5)_2O$ is 51.

NOTICES OF BOOKS.

A Safe Course in Experimental Chemistry. By W. T. BOONE, B.A., B.Sc. The University Tutorial Series. London: W. B. Clive, 1904. Pp. 180.

We are not sure that the author has been very happy in his choice of a title for this book; it appears from the preface that the experiments "could with few exceptions be performed at home with perfect safety"—and hence we presume the title, "A Safe Course"; but is not this accentuating rather unnecessarily the very slight amount of danger attached to a simple course of experimental chemistry for beginners?

As for the arrangement and compilation of the book, we have no criticism to offer. It is well adapted for its avowed purpose, as set forth in the syllabus issued by the Incorporated Association of Head-masters, viz., "to train students to solve simple problems by experiment, to work accurately, and with a clearly defined purpose, and to reason from observation." The book has a good index.

Experiments on the Metabolism of Matter and Energy in the Human Body, 1900-1902. By W. O. ATWATER, Ph.D., and F. G. BENEDICT, Ph.D. Washington: Government Printing Office, 1903. Pp. 357.

The experiments here reported form part of a series which is in progress at Middletown, Conn., in co-operation with the Storrs Agricultural Experiment Station and Wesleyan University. The present Bulletin includes, along with the details of the experiments, an account of a number of important improvements in apparatus and method not hitherto described.

The experiments yield valuable data regarding the conservation and transformation of matter and energy in the body, the demands of the body for nutriment, the effects of muscular work upon such demand, and the actual nutritive values of different food materials and their ingredients.

The results of these experiments are summarised with those of thirty-four previously reported, making fifty-five experiments in all.

The whole inquiry rests upon the principle that the transformations of matter and energy in the body take place in accordance with the two fundamental laws of the conservation of mass and the conservation of energy; and the conclusion drawn from the experiments is that the law of the conservation of energy held good as regards the men who were studied. For practical purposes, therefore, we are warranted in assuming that the law obtains in general in living organisms, as there is every reason to believe that it must.

Wilhelm Ostwald. By P. WALDEN. Leipzig: Wilhelm Engelmann, 1904.

Last year saw the publication of more than one volume in celebration of Prof. Ostwald's Jubilee, of which books this short biography is a very good specimen. It contains a graphic picture of the life and character of a man of the most marked individuality. The difficulty of the task with which the biographer has to grapple is very materially augmented owing to the fact that the great master is happily still with us, but the author has satisfactorily coped with this difficulty, and has produced a very attractive and appreciative little volume. The short section on Ostwald's

artistic talents will probably contain much that is new to many to whom he is not known personally, a heliogravure of one of his pastels as well as an excellent portrait being included.

Grundlinien der Anorganischen Chemie. ("The Principles of Inorganic Chemistry"). By W. OSTWALD. Second Edition. Leipzig: Wilhelm Engelmann, 1904.

The facts that in three years the first edition, consisting of 4000 copies, of this work has been exhausted, and that English and Russian translations have appeared, show plainly that Ostwald's views regarding instruction in pure chemistry have strongly recommended themselves to a large number of teachers and lecturers in spite of a good deal of vehement opposition at one time.

In this edition no fundamental alterations have been made. Beyond carefully revising the whole of the text and re-modelling in places where greater detail of explanation seemed necessary, the author has been content to issue the work in the same form as at first, and there can be no doubt that the more this method of introducing the learner to the study of chemistry is known the greater will be the demand for this text-book.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 17, April 25, 1904.

Atomic Weights of Oxygen and Hydrogen and the Probable Value of their Atomic Relation.—Ph. A. Guye and Ed. Mallet.—The final value resulting from the authors' careful determinations is $O = 15.8787$ given $H = 1$, or $H = 1.00764$ for $O = 16$ (with an error of $1/80,000$ only on the most discordant of the mean values). The weight of a litre of normal oxygen (1.42886 gm.) and of hydrogen (0.089875 gm.) is also determined.

Experimental Researches relative to certain Cyclic Amines.—P. Lemoult.—The author measures experimentally the heats of combustion of the following cyclic amines:—

Xylidine	At constant volume . .	1111.42 cal.
	pressure . .	1112.70 "
Monoethylaniline . .	volume . .	1125.60 "
	pressure . .	1126.88 "
Anisidine	volume . .	927.29 "
	pressure . .	928 "
α -Naphthylamine . .	volume . .	1268.78 "
	pressure . .	1269.78 "
β -Naphthylamine . .	volume . .	1266.5 "
	pressure . .	1267.5 "

Formation of Hydrogen Silicide, SiH_4 , by Direct Synthesis from its Elements.—A. Dufour.—Hydrogen and silicon unite directly, but in very small quantities, at a temperature above that of fusion of silicon, giving hydrogen silicide, SiH_4 . This result is in agreement with the endothermic formation of hydrogen silicide.

Lead-aluminium Alloys.—H. Pécheux.—The author prepares three alloys of lead and aluminium, containing 93, 95, and 98 per cent of aluminium respectively. He finds the density of these and examines their properties. They are all unattacked by moist air at their melting-points, but are readily attacked by most acids. Distilled water has no action on them either at 0° or 100°.

Colloidal Gold.—M. Hanriot.—Henrich described, under the name of colloidal gold, solutions which he obtained by treating gold chloride by certain reducing phenols, such as pyrocatechin and hydroquinone. The author prepares one of these substances from pyrocatechin in the form of a blue powder, slightly soluble in pure water, but insoluble in a slight excess of sulphuric or nitric acid. It dissolves in alkalis easily, especially in ammonia. An analysis of the substance dried at 40° shows—Water driven off at 100°, 2.04; water lost at a red heat, 6.31; gold (direct estimation), 91.53; SO₃, 0.39. He discovers also the curious fact that colloidal gold does not dissolve in mercury.

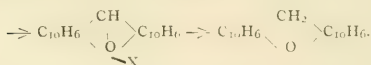
A New Indicator: its Employment for the Research of Boric Acid in general, and particularly in Alimentary Substances.—Lucien Robin.—The author prepares an indicator from the flowers of mimosa. It is of a pale yellow colour, but when a drop is added to 10 c.m. of distilled water no perceptible tint is observed. It behaves in the same manner as phenolphthalein, becoming bright yellow on the addition of alkalis and losing its colour when neutralised by acids. It is especially useful for titrating boric acid.

Action of Magnesium and the Organo-magnesium Compounds on Bromophenol.—V. Grignard.—Under normal conditions the magnesium derivative of bromophenol is not stable, nor are the analogous magnesium compounds derived from the ether oxides of arylaliphatic phenols. The author believes that the union of the aromatic organo-magnesium compounds—and especially the phenolic with bromophenol, or with compounds of the same type as phenoxybromopropane-1—3, for example—will enable him to effect the synthesis of the primary halogen arylaliphatic compounds, whose preparation up to the present has been impossible when the lateral chain under consideration possesses more than an atom of carbon. He actually examines this generalisation.

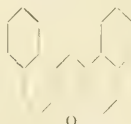
Researches on the Dinaphthopyranic Series.—R. Fosse.—The product of chromic oxidation of ethylidene di-*β*-naphthylene oxide does not appear to be a dinaphthopyrone. On contact with alkaline carbonates, the di-*β*-naphthyl carbonate decomposes into CO₂, *β*-naphthol, and dinaphthopyrane, according to the equation



Starting with *β*-naphthyl carbonate, CO₂(C₁₀H₇)₂, the author obtains the following series of transformations:—Dinaphthopyrone (fuses 194°), dinaphthopyranol (fuses 145°), salts of dinaphthopyryl, dinaphthopyrane (fuses 201°).



All these bodies have the following molecular structure:—



Oxyctronic Lactone and the γ -Substituted Crotonic Acids.—M. Lespieau.—By fixing two atoms of chlorine or bromine on to vinylacetic acid, CH₂=CH—CH₂—CO₂H, the author obtains substituted

butyric acids in β and in γ , by the aid of which he prepares the γ -substituted crotonic acids.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 15.

The Existence of Arsenic in Bird's Eggs.—Gabriel Bertrand.—As a result of his previous researches on the normal arsenic in the organism, the author has come to the conclusion that this metalloïd—like carbon, sulphur, and phosphorus—is a constant element of the living cell, and that, instead of being localised in a few organs, it is, on the contrary, in all the tissues. If this is the case, arsenic should be found in the organism at all periods of life—in the embryonic cells as in the adult. It should be found therefore in bird's eggs, where the embryo is forced to develop without drawing on the outside world for any particle of arsenic it may need. For the purpose of testing this hypothesis the author has made three series of experiments. The first, in a measure preliminary, on ordinary eggs of commerce or "shop eggs"; the two others on eggs laid by hens kept specially under observation and carefully fed since the previous generation. In the end, arsenic was found in all the eggs used, both in the yolk, the white, the membrane, and the shells, in quantities varying from 5.0 to 0.5 thousandths of a milligram. per egg, according to the part of the egg examined. It is the yolk which is the richest in arsenic; it contains from one-half to two-thirds of the total amount present in the egg.

The Decomposition of Carbonate of Lithium by Heat.—P. Lebeau.—Already noticed.

Commercial Silicated Manganeses.—P. Lebeau.—Already noticed.

Silicides of Chromium.—P. Lebeau and J. Figueras.—Already inserted in full.

New Method for the Qualitative and Quantitative Analysis of Osmides of Iridium.—MM. Leidié and Quennessen.—Already inserted in full.

New Method for the Estimation of Halogen Bodies in Organic Compounds.—H. Baubigny and G. Chavanne.—Already noticed.

New Method for the Estimation of Organic Matters in Waters, and particularly in those which contain Chlorides and Bromides.—C. Lenormand.—Already inserted in full.

Colloidal Silver.—M. Hanriot.—Already noticed.

The Benzoylised Derivatives of Hydrazobenzene and of its Homologues.—P. Freundler.—Already noticed.

The Sugar in the Milk of the Buffalo Cow.—Ch. Porcher.—A controversial paper, in which the author disputes the statement made by Messrs. Pappel and Richmond, that the sugar in the milk of the buffalo cow is not lactose, but a special sugar to which they gave the name of tewfikose. He finds that this sugar answers to all the reactions of lactose.

The Carbohydrates of Barley, and their Transformations during Germination.—L. Lindet.—A long paper, not suitable for abstraction.

Distribution of some Organic Substances in the Geranium.—Eug. Charabot and G. Laloue.—The authors have found that in the geranium the volatile acids diminish as we pass from the leaf to the stalk; further, the terpenic compounds of the geranium are entirely localised in the leaf. Knowing now that these compounds are produced by the leaf and do not circulate through the stalks and stems, we can understand perfectly why the flowers of the geranium have no odour.

A New Washer and a New Safety Tube.—H. Vigreux.—This paper cannot be followed without the accompanying diagram.

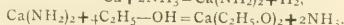
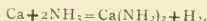
MISCELLANEOUS.

Petroleum Acts.—It has recently come to our knowledge that attempts are being made by officers of local authorities to apply the legal test for petroleum to samples of liquid metal-polish, and we have satisfied ourselves by experiment that the results thus obtained are sometimes entirely misleading, as they do not represent the temperature of the portion of the liquid from which inflammable vapour is being evolved. In carrying out the test prescribed by the Petroleum Act, 1879, the sample under examination is slowly heated in a closed cup, and the temperature is indicated by a thermometer, the bulb of which is immersed in the liquid in the centre of the vessel. In these circumstances the heat communicated to the sample through the walls of the cup creates in such a liquid as petroleum convection currents, and through the circulation thus set up the temperature of the contents of the cup is equalised and the thermometer correctly indicates the temperature at which inflammable vapour is evolved by the liquid. On the other hand, if the sample contains solid matter in suspension, as is the case with the liquid metal-polish in question, the formation of convection currents is interfered with, and the surface of the liquid from which inflammable vapour is evolved, acquires a higher temperature than that of the portion in contact with the bulb of the thermometer. Thus, as we have ascertained experimentally, the thermometer may indicate a temperature of 59° F. when the temperature of the surface is 83° F., and a sample may be erroneously reported as having a flash-point below the legal limit of 73° F., when the true flash-point is far above the limit. No doubt this would have been provided for when the Act was passed if at that time the need for applying the test to such substances had been foreseen, but it was not until judgment in the case of the London County Council *v.* Holtzapfel's Compositions Company, Limited, was given in 1899 that mixtures containing petroleum were held to be petroleum within the meaning of the Acts. In our "Handbook on Petroleum," published in 1901, we referred on page 90 to the necessity for a stirrer in the oil cup when the test specified in the Petroleum Act is employed for the testing of paints and other substances containing petroleum, and when opportunity occurs for a revision of the law this addition will doubtless be legalised. We are, however, of opinion that in the meantime authorities charged with the administration of the Petroleum Acts should be made aware of the circumstances we have referred to, and that testing officers should take steps to ascertain the true flash-point of samples of liquid metal-polish or other substances which are not thoroughly liquid, and therefore cannot be satisfactorily tested in precise accordance with the directions given in the schedule to the Act. In many instances it may be possible to obtain a sample of the petroleum used in the substance, or the solid matter present in the sample can be removed by straining or filtration, care being taken to avoid loss of the more volatile constituents by evaporation, when the separated liquid can be tested in the prescribed manner. The liquid should not, however, be separated by distillation, as this operation may yield a distillate of lower flash-point than that of the petroleum with which the mixture was made. For guidance in determining whether there has been any infraction of the law, the sample may also be tested in an apparatus provided with an efficient stirrer. In any case of doubt as to the true flash-point of the material we would suggest that reference should be made to H.M. Inspectors of Explosives at the Home Office, who will be prepared to give advice as to the course which should be adopted.—(Signed) J. H. THOMSON, Captain, H.M. Chief Inspector of Explosives; BOVERTON REDWOOD, Adviser on Petroleum to the Home Office; April 30th, 1904.

Silicic Acid (II).—E. Jordis and E. H. Kanter.—The preparation of a pure colloidal solution of silica is difficult.

Contrary to what has been stated by Graham, the authors have only been able to obtain very dilute solutions by his method. The proportion, 12 per cent, given by him (*Comptes Rendus*, vol. lix., p. 174), appears to be mistaken, for as soon as the amount reaches 1.8 to 2.0 per cent a deposit of gelatinous silica is formed. This figure is close to that obtained by Grimaux (*Comptes Rendus*, vol. xcvi., p. 1485), who succeeded in obtaining a solution of silica containing 2.26 per cent, by the decomposition of methyl ether, $\text{Si}(\text{OCH}_3)_4$, by boiling water. By boiling gelatinous silica with water in a flask with a vertical condenser, we obtain solutions, the strength of which may reach 0.15 per cent, but it appears that this relatively high percentage is only due to traces of foreign matters, as the same silica boiled afresh only goes into solution in much slighter proportions (0.047 to 0.027 per cent). Grimaux's figure is too high for the same reasons. On repeating his experiments the proportion of silica was lowered to 0.1 per cent, and, further, the silica obtained by evaporation and calcination was blackened on account of the presence of organic matter. If, during the preparation by means of dialysis, we add a drop of acid or alkali, the proportion of silica increases to 10 per cent. In conclusion, silica does not give a pure hydrosol, but must be looked upon as an amphoteric substance.—*Zeit. Anorg. Chem.*, vol. xxxv., p. 16.

Action of Calcium on Alcoholic Ammonia.—G. Doby.—Ethylate of calcium, which has not yet been prepared in a pure state, takes rise in the reciprocal action of ammonia gas, calcium, and ethylic alcohol. Amide of calcium is first formed, and this is then transformed by the alcohol into ethylate with the regeneration of the ammonia,—



Ethylate of calcium crystallises with 2 molecules of alcohol, which can be eliminated at about 50°. At the same time as the ethylate, $\text{Ca}(\text{C}_2\text{H}_5\text{O})_2 + 2\text{C}_2\text{H}_5(\text{OH})$, is formed, the action of the ammonia and the alcohol on the calcium gives another compound in hexagonal crystals having the formula $\text{CaO}_3\text{C}_2\text{H}_6\text{O}$. These crystals are apparently identical with those obtained by De Forcrand (*Comptes Rendus*, vol. cxix., p. 1266), and are only formed on account of the presence of a little moisture. Ethylate of calcium occurs in white needles, soluble in hot alcohol; the solution becomes brown on contact with the atmospheric oxygen; when exposed freely to the air it gives the carbonate. On contact with water, the anhydrous ethylate is decomposed into $\text{Ca}(\text{OH})_2$ and alcohol. The same ethylate is also formed by the action of hydride of calcium upon alcohol, according to the equation, $4\text{C}_2\text{H}_5\text{—OH} + \text{CaH}_2 = (\text{C}_2\text{H}_5\text{O})_2\text{Ca} \cdot 2(\text{C}_2\text{H}_5\text{—OH}) + 2\text{H}_2$.—*Zeit. Anorg. Chem.*, vol. xxxv., p. 93.

Suboxide of Phosphorus, and the Solubility of Red Phosphorus in Alcoholic Aqueous Potash.—A. Michaelis and K. Von Arend.—After having announced that the suboxide of phosphorus of Michaelis and Pitsch was impure amorphous phosphorus, D. L. Chapman and F. A. Lidbury confirmed the existence of this suboxide. They announced, further, the curious fact that commercial red phosphorus was soluble in alcoholic aqueous potash. Their conclusions on this point are as follows:—1. Red phosphorus, as well as ordinary crystalline phosphorus, and the amorphous phosphorus obtained by heating phosphorous acid with trichloride of phosphorus, is insoluble in alcoholic aqueous alkali. 2. If red phosphorus is ground for a long time with water, it becomes partially oxidised to the state of suboxide, and to a very slight extent to the state of acids of phosphorus. 3. In the absence of water (toluene, sulphide of carbon) a portion of the ground-up phosphorus becomes transformed into ordinary phosphorus which, as we know, is soluble in the alkalis.—*Liebigs Annalen*, vol. cccxxxv., p. 361.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Colouring Varnish.—I have recently been trying to colour an essential oil (rosemary) varnish with alizarine—red, brown, and purple. For the red I used sodium carbonate and alum; for the brown, oxide of iron; and for the purple, caustic potash. I am highly pleased with these colours, but I find that the salts form an emulsion with, or saponify, the gums and precipitate them, but not the alizarine. Therefore what I want to find out is how to get these alizarine or madder colours (which are practically the same) into the varnish without at the same time emulsifying or precipitating the gums.—CHAS. E. POLLARD, Cape Town.

MEETINGS FOR THE WEEK.

TUESDAY, 31st.—Royal Institution, 5. "The Solar Corona," by H. F. Newall, F.R.S., &c.

Society of Arts, 4.30. "The Economic and Industrial Progress and Condition of India," by J. E. O'Connor, C.I.E.

WEDNESDAY, June 1st.—Society of Public Analysts, 8. "The Analysis of Condensed Milk," by J. R. P. Harrison. "Roasted Beetroot," by E. G. Clayton. "A Collection of Readings with the Zeiss Oleo-butyrometer," by William Chataway and C. G. Moor. "Note on the Estimation of Sugars and Starch in Vegetable Substances," by John S. Ford.

THURSDAY, 2nd.—Royal Institution, 5. "Literature and the State," by H. G. Wells, B.Sc.

Chemical, 8. "Iso-Nitrosocamphor," by M. O. Forster. "Imino-ethers and Allied Compounds corresponding with the Substituted Oxamic Esters," by G. D. Lander. "Action of Heat on α -Hydroxycarboxylic Acids—Part I., α -Hydroxy-stearic Acid," by H. R. Le Sueur. "The Basic Properties of Oxygen—Additive Derivatives of the Halogen Acids and Organic Compounds and the Higher Valencies of Oxygen—Asymmetric Oxygen," by E. H. Archibald and D. McIntosh.

FRIDAY, 3rd.—Royal Institution, 9. "The Development of the Theory of Electrolytic Dissociation," by Prof. Svante Arrhenius.

SATURDAY, 4th.—Royal Institution, 3. "Spitsbergen in the Seventeenth Century," by Sir William Martin Conway.

UNIVERSITY COLLEGE OF SOUTH WALES
and MONMOUTHSHIRE, Cardiff.

The Council of the College invite applications for the following Posts:—

1. ASSISTANT LECTURER in MATHEMATICS.
2. DEMONSTRATOR and ASSISTANT LECTURER in CHEMISTRY.
3. DEMONSTRATOR and ASSISTANT LECTURER in PHYSICS.
4. DEMONSTRATOR and ASSISTANT LECTURER in PHYSIOLOGY.
5. DEMONSTRATOR and ASSISTANT LECTURER in BOTANY.

In the case of the appointment in Physics, preference will be given to candidates who have some knowledge of the technical applications of Electrical Science.

Further particulars may be obtained from the undersigned, to whom applications, with testimonials (which need not be printed), must be sent, endorsed on the outside with the title of the Department in which the application is made, on or before MONDAY, JUNE 20th, 1904.

J. AUSTIN JENKINS, B.A.,
Registrar.

University College, Cardiff,
May 16, 1904.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC,
[As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET
LEAD and PIPE, LITHARGE, &c.

E. GEORGE & SONS,
BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.

Are OPEN to PURCHASE Complete Sets
or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1858 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.

IMPERIAL
COLLEGE OF CHEMISTRY,
49 & 51, IMPERIAL BUILDINGS, LUDGATE CIRCUS, E.C.

Principal—FREDERICK DAVIS.

PRACTICAL AND THEORETICAL TUITION
In Botany, Chemistry, Pharmacology, and Therapeutics for
All Medical and Science Examinations.
Especially Course of Instruction in Therapeutics, Pharmacology,
and Microscopy for Institute of Chemistry Exam.

THE CHEMICAL NEWS
AND
JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post
free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 10 words to line)	0	3	6
Each additional line	0	0	6
Whole column	1	15	0
Whole page	3	0	0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

ABSOLUTE ALCOHOL,
FREE FROM DUTY,
FOR SCIENTIFIC AND RESEARCH WORK IN LABORATORIES:
To be obtained from
HUGO LORENZ,
7-8, Idol Lane, Great Tower St., London, E.C.,
Licensed Trader in Alcohol and Spirits of Wine,
Stock kept in suitable packages ready for immediate use.

CONVEYING
AND
ELEVATING
PLANT.

Write for New Catalogue.

GIBBONS BROS., Ltd.,
DUDLEY, WORCS.

LONDON OFFICE—132/3, Palace Chambers, Westminster, S.W.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2323.

THE BOILING-POINTS OF HOMOLOGOUS COMPOUNDS.

By HUGH RAMAGE, B.A., St. John's College.

THE relations between certain properties of elements and their atomic masses have been described by the writer in *Roy. Soc. Proc.*, 1902, lxx., pp. 1 and 303. These relations were discovered by a study of diagrams drawn with the physical constants as abscissæ and the atomic masses—or the squares of these—as ordinates. This graphical method does not appear to have been employed by other workers, except in the simplest form, for showing that the properties are periodic functions of the atomic masses.

The method has been extended to other properties of the elements, and also to those of compounds. Amongst the latter, the boiling-points offer the most complete data, and in addition furnish constants which are amongst the least affected by other factors—such, for instance, as association of the molecules,—and, moreover, they are, especially amongst organic compounds, the most accurately determined of the physical constants. A study of the boiling-points of many substances has been made, and some facts relating to the boiling-points of homologous compounds will be dealt with in this paper.

Professor James Walker has given a general formula, $T = aM^b$, for the boiling-points of homologous compounds (*Trans. Chem. Soc.*, 1894, lxx., 193, 725), in which T is the boiling-point in absolute degrees, M is the molecular weight, and a and b are constants for each series. He applied it to several series, and amongst them to the normal paraffins from C_7H_{16} to $C_{16}H_{34}$. He found that it did not apply to the alkyl bromides and iodides, the normal alkylamines, and the normal ketones and aldehydes. He also stated that no formula of this type could possibly be applied to the alcohols.

It was observed when drawing the curve through the boiling-points of the paraffins that it would, if produced below methane, pass very near to the position of hydrogen; it seemed at first, when using the older figure for methane (113°), that hydrogen might be regarded as a member of the series. It was, however, found by drawing a diagram with the logarithms instead of the numbers, that hydrogen did not fall on the curve, but it fell near it. The change from H_2 to CH_4 is not very different from what it would be were hydrogen the first member of the series.

In referring to the ten hydrocarbons to which his formula applies, Walker remarked—"In this particular case the formula is unusually simple, for the constant b becomes equal to 0.5, the curve of boiling-points being therefore a true parabola." He does not discuss the point further. The curve to Walker's formula was drawn on the diagram, and in studying the two curves it appeared probable that the simple formula only applied exactly to the CH_4 chain linkage, and that the influence of the terminal hydrogen atoms was either a constant in the higher members of the series, or it was so small that it might be disregarded. The influence of these terminal atoms increases as the chain shortens and the atoms approach each other until, in methane, the diagram indicates we practically have the effect of two CH_2 groups. This work has suggested a modification of the formula which applies to the series from methane to hexadecane.

The new formula is $T = a \{M(1 - 2^{-n})\}^{\frac{1}{2}}$; where n is the number of carbon atoms in the molecule. The constant a is the same as Walker used. It may, however, be expressed as a function of the pressure, and it is given approximately for pressures of 15, 30, 50, 100, and 760 m.m. by the equa-

TABLE I.

Paraffin.	Observed boiling-point.	Calculated boiling-point	Differences
CH_4	108°3	105°7	-2°6
C_2H_6	180°0	177°3	-2°7
C_3H_8	228°0	231°9	+3°9
C_4H_{10}	274°0	275°6	+1°6
C_5H_{12}	309°3	312°2	+2°9
C_6H_{14}	342°0	343°9	+1°9
C_7H_{16}	371°4	372°3	+0°9
C_8H_{18}	398°5	398°3	-0°5
C_9H_{20}	422°5	422°5	0
$C_{10}H_{22}$	446°0	445°2	-0°8
$C_{11}H_{24}$	467°5	466°8	-0°7
$C_{12}H_{26}$	487°5	487°3	-0°2
$C_{13}H_{28}$	507°0	507°0	0
$C_{14}H_{30}$	525°5	526°0	+0°5
$C_{15}H_{32}$	543°5	544°2	+0°7
$C_{16}H_{34}$	560°5	561°9	+1°4

TABLE II.

Alcohol.	Observed boiling-point.	Calculated boiling-point.	Differences.
Methyl	337°7	331°1	-6°6
Ethyl	351°3	351°1	-0°2
Propyl	370°4	370°8	+0°4
Butyl	390°0	390°5	+0°5
Amyl	411°0	410°3	-0°7
Hexyl	430°0	430°0	0
Heptyl	449°0	449°8	+0°8
Octyl	469°0	469°4	+0°4

TABLE III.

Aldehyde.	Observed boiling-point.	Calculated boiling-point.	Differences.
Formic	252°0	267°0	+15
Acetic	293°8	294°0	+0°2
Propylic	321°8	321°0	-0°8
Butylic	348°0	348°0	0
Amylic	376°4	375°0	-1°4
Capric	401°0	402°0	+1°0
Ketone.			
Acetone	330°0	335°0	+5
Di-ethyl	376°0	376°0	0
Di-propyl	417°0	417°0	0
Di-butyl	—	458°0	—
Di-amyl	499°0	499°0	0
Di-hexyl	536°0	540°0	+4
Methyl-ethyl	354°0	355°5	+1°5
Methyl-propyl	375°0	376°0	+1

tion $a = 23.5 P^{0.07}$; where P is the pressure. Calculated from the first sixteen members of the series for a pressure of 760 m.m., its mean value is 37.3775—a figure which is practically identical with that calculated by the simpler formula (37.38) from the higher members of the series. When $n = 11$ and upwards the two formulæ give the same results to the first decimal place. Table I. gives the observed and calculated numbers and the differences between them.

The simple formula gives a difference of +4.2° for methane and of +24.7, 19.9, 10.6, 7.9, 4.6, and 2.4° respectively for the succeeding members of the series.

Normal Alcohols.

The line which passes through the points given by the molecular weights and boiling-points of water and the alcohols, is sharply curved at the beginning, and then it becomes almost straight. The following linear equation gives the boiling-points of the alcohols:—

$$T = 286.2 + 1.41 M.$$

Table II. gives the observed and calculated numbers in absolute degrees.

Aldehydes and Ketones.

The boiling-points of these are also given by linear equations—

1. Aldehydes . . . $T = 209.14 + 1.9286 M$.
2. Ketones . . . $T = 250.07 + 1.4643 M$.

The observed and calculated numbers, in absolute degrees, are given in Table III.

It is worthy of remark that the difference in boiling-points of two ketones differing by CH_2 is about 41.0° , and this is the difference between the first constants in the above equations.

The influence of the oxygen atoms in the compounds given in the last two tables is very marked, as it also is in the acids. The curve representing the acids is irregular, and it indicates that the boiling-points of the lower members are abnormal, due doubtless to the association of their molecules, whilst the boiling-points assume a normal value in the higher members of the series.—*Proceedings of the Cambridge Philosophical Society*, vol. xii., Part 5.

FURTHER EXPERIMENTS ON THE PRODUCTION OF HELIUM FROM RADIUM.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.,
and
FREDERICK SODDY, M.A.

(Concluded from p 258).

Experiment 5.—The former experiment was repeated, this time with a regular capillary tube, of which the volume per centimetre was 0.24 cub. m.m. It was regular in bore, and the depression due to capillarity was 56.2 m.m. of mercury. It was heated, as well as the bulb in which the emanation was to be condensed, to incipient redness during evacuation. The emanation was introduced, the accompanying hydrogen pumped off, and the liquid air jacket removed. The volume of the emanation was read at once, at different pressures. The following table gives the lengths of the capillary tube, the corresponding volumes, the pressures corrected for capillarity, and the products of volume into pressure:—

Length of tube.	Volume in cub. m.m.	Pressure in m.m.	Volume $\times$ pressure.
6.80	0.163	132.4	21.6
2.30	0.0552	333.4	18.4
1.55	0.0372	518.1	19.3
1.20	0.0288	644.8	18.6
0.95	0.0228	765.8	17.5
2.55	0.0612	309.2	18.9
11.90	0.372	55.3	20.6

The mean value of the product is 19.3 , and the volume at normal pressure 0.0254 cub. m.m. The same afternoon, numerous readings were taken, and it was found that the sticking of the mercury in the capillary tube made it difficult to ascertain the true volume. As the pressure, however, was first raised and then lowered, the mean cannot be far from the truth. Now, a most remarkable circumstance must be chronicled. Whereas the emanation in the previous experiment contracted during its whole life, in this experiment a regular expansion was observed, rapid at first, and slowly falling off from day to day. Between five minutes past 1 o'clock and 7 o'clock, the pressure being kept constant at 55.3 m.m., the value of P.V. increased from 20.6 to 48.4 . This was on January 20th. On the 21st, the P.V. had increased to 71.2 , and remained fairly constant all day, and three small bubbles appeared in the thread of mercury, below the level of the emanation. On the 22nd, the value of P.V. had diminished to 50.5 , and the volume of the bubbles had increased to 2.7 m.m. length in the tube. On the 23rd, the emanation occupied

practically the same volume, but the length of the bubbles had increased to 4.1 m.m. The presence of these bubbles made it impossible to obtain correct readings, for the "sticktion" of the mercury was much increased. On the 25th, P.V. had further diminished to 51.2 , and the length occupied by bubbles had increased to 5.5 m.m. On February 3rd, the bubbles were united with the emanation; the value of P.V. was 132.5 and the volume of the gas under normal pressure, 0.174 cub. m.m. On the 9th, the P.V. had increased to 166 , and the volume at normal pressure to 0.224 cub. m.m. Lastly, the volume of the gas was measured on the 12th at atmospheric pressure; it amounted to 0.262 cub. m.m. The level of the mercury was then lowered, and the gas pumped out; it showed a brilliant spectrum of helium. The tube was then heated, and the volume of the absorbed gas was 0.103 cub. m.m. at atmospheric pressure; it, too, showed the helium spectrum, but the tube punctured before this could be confirmed.

These results are somewhat inexplicable in the light of the former experiment. More stringent precautions had been taken to free the capillary tube from gas in the second experiment than in the first, and yet bubbles appeared below the surface of the mercury. It may be that owing to the quality of the glass of which the first tube was made, the helium found means to enter into its substance more easily than into that of the second. But at any rate, the volume produced is of the same order, as the following considerations will show.

On the view that the emanation results from a definite fraction of the radium disintegrating per second, this fraction can be calculated from the volume of the emanation, and the time of accumulation. The emanation accumulates until the rate of production is balanced by the rate of disappearance, and then the quantity remains constant. Let Q_∞ be the equilibrium quantity, and Q_t the quantity present after time t ,—

$$Q_t / Q_\infty = 1 - e^{-\lambda t},$$

where t is expressed in seconds, and λ is a constant representing the proportion of the emanation changing per second, and equals $1/463,000$ (Rutherford and Soddy, *Phil. Mag.*, 1903, [6], vol. v., pp. 445 and 576). The radium bromide employed weighed about 60 milligrams. Assuming that the compound contained about half its weight of the element (radium, 225; bromine $+ 2\text{H}_2\text{O}$, 196), the quantity of radium may be taken as about 0.03 gm. In the first experiment, the time of accumulation t was eight days = $691,200$ seconds; Q_t therefore equals $0.775 Q_\infty$. The volume taken (0.027 cub. m.m.) in the first experiment was that at the end of the first day, and a correction must be applied to allow for the amount that had changed in this interval. The quantity remaining after the lapse of one day is 0.83 of the initial quantity. The volume, 0.027 cub. m.m., is therefore—

$$0.83 \times 0.775 Q_\infty = 0.643 Q_\infty.$$

The average life of the particle in a system in which a constant fraction λ of the number of particles changes per second can be shown to be $1/\lambda$. The equilibrium quantity, Q_∞ , is the quantity produced in the period of average life of the atom of the emanation, or $Q_\infty = Q_0 \lambda = 463,000 Q_0$, where Q_0 is the quantity produced per second. And $0.643 Q_\infty = 297,830 Q_0$. The volume of Q_0 is thus $0.027 \times 297,830 = 0.9 \times 10^{-7}$ cub. m.m. This is in the case of 0.03 gm. of radium; 1 gm. of radium, therefore, produces 3×10^{-6} cub. m.m. of emanation per second.

Since the emanation resembles the gases of the argon family in chemical inertness, its molecule is probably monatomic, and its atomic weight must be twice its density in terms of hydrogen as unity. The density is not accurately known; but diffusion experiments indicate a value of about 80. The atomic weight being therefore in the neighbourhood of 160, not more than one atom of emanation can be produced from one atom of radium. To

* A Paper read before the Royal Society, April 28, 1904.

determine the ratio between the quantity of emanation and the quantity of radium producing it, it is necessary to know the volume that would be occupied by the radium in the form of monatomic gas. This is for 1 grm. of radium ($2 \times 1120 \cdot 225 \div 0 \cdot 1$ litre = 10 cub. m.m.). One grm. of radium produces 3×10^{-6} cub. m.m. of emanation per second, and if one atom of radium produces one atom of emanation, then λ , the proportion of the radium changing per second, is 3×10^{-11} . The proportion changing per year is $9 \cdot 5 \times 10^{-4}$; thus slightly less than one-thousandth part changes per year. The average life of the radium atom is $1/\lambda = 3 \cdot 3 \times 10^{10}$ seconds = 1050 years.

In the second experiment, the emanation was accumulated six days, and measured $0 \cdot 0254$ cub. m.m. In this case,—

$$Q_1 = 0 \cdot 674 Q_2 = 312 \cdot 060 Q_0$$

and $Q_2 = 0 \cdot 51 \times 10^{-7}$ cub. m.m.; $\lambda = 2 \cdot 4 \times 10^{-11}$, and $1/\lambda = 1250$ years. The mean of the two experiments, therefore, gives for 1 grm. of radium (element) $Q_0 = 2 \cdot 85 \times 10^{-8}$ cub. m.m.; $Q_{20} = 1 \cdot 3$ cub. m.m., $\lambda = 2 \cdot 85 \times 10^{-11}$, and $1/\lambda = 1150$ years.

Rutherford and Barnes (*Phil. Mag.*, 1904, [6], vol. vii., p. 202) have shown that 75 per cent. of the total heat-evolution of radium which has reached its equilibrium state is derived from the emanation and its subsequent products of change. Since 1 grm. of radium evolves 100 calories per hour (Curie), $1 \cdot 3$ cub. m.m. of emanation emit 75 calories per hour. The total quantity of heat H emitted during the complete change is given by multiplying h the emission per second, by the average life of the emanation in seconds, thus giving $H = h/\lambda = 9546$ calories. One c.c. of emanation would therefore emit $7 \cdot 4 \times 10^6$ calories during its complete change. A c.c. of hydrogen and oxygen in the proportion required to form water evolve 204 calories on explosion, or a quantity 3,600,000 times less than is emitted by an equal volume of the radium emanation. If the density of the emanation is assumed to be 100, the ratio of the energies emitted by equal weights of emanation and of water is 216,000 to 1.

The total quantity of energy evolved during the change of 1 grm. of radium is given by multiplying the energy emission per second by the average life of the radium atom in seconds, and is 10^7 calories. The energy evolved in the formation of 1 grm. of water is $3 \cdot 8 \times 10^6$ calories; hence the ratio is again about 250,000 to 1.

The volume of Q_{20} , the equilibrium quantity of emanation produced by 1 grm. of radium, was theoretically calculated by Rutherford (*Nature*, August 20, 1903) from the energy emitted by radium per second, and the energy of the α -particle, as calculated from its mass and its velocity. By making certain assumptions about to be considered, he deduced that Q_{20} must lie between $0 \cdot 6$ and $0 \cdot 06$ cub. m.m. The maximum estimate, which is almost exactly one-half the experimental value found by us, was based on the assumption that the whole, and the minimum estimate on the assumption that only one-tenth, of the energy of disintegration is manifested in the kinetic energy of the α -particle expelled. It was further assumed that only one α -particle was expelled from each atom, at each disintegration accompanied by α -radiation that is known to occur. If more than one α -particle is expelled at each disintegration, the theoretical estimate must be correspondingly reduced. Since the experimental value exceeds the maximum theoretical estimate, it follows that there are now direct experimental reasons for believing that—

1. Only one α -particle is expelled from the atom at each disintegration.
2. The greater part of the energy of disintegration appears in the form of kinetic energy of α -radiation.
3. The emanation is a monatomic gas.

It must be remembered that the experimental value is necessarily a maximum value; for if any impurity were present with the emanation, it would increase the volume measured.

ON THE EMANATION SUBSTANCE (EMANIUM).*

By F. GIESEL.

THE investigation of the spark spectrum of the emanation substance, which Runge and Precht very kindly undertook, has proved that the substance consists essentially of lanthanum with a little cerium. Thorium, barium, and radium were not present. New lines could not be observed, it being impossible to say anything definite on this point owing to the enormous number of lines.

The anhydrous chloride or bromide (to a less degree the sulphate) which phosphoresces spontaneously, show a discontinuous phosphorescence spectrum, consisting of three lines, from about the red to the blue-green, at approximately equal distances.† The determination of the position of the lines is made much more difficult owing to the feebleness of the light, but the determination must be made by the photographic method in order to see whether the spectrum of a new rare earth is obtained.

During a further period of observation lasting one year the following results relating to the properties of the "emanation substance" have been obtained.

Glass vessels in which the substance has been kept for some months become violet coloured up to the level to which they were filled. Paper becomes brown, and is destroyed.

First of all I convinced myself that the activity of the solid salts suffers absolutely no further change as soon as the maximum has been reached, which occurs after about one month after they have separated out from the solution. The conditions are exactly similar to those which I have described for radium (*Ann. d. Phys. u. Chem.*, 1899, lxi., 92). The original (β -) radiation is smaller the longer the substance is kept in solution and the more dilute it is.

This behaviour characteristic of the primarily active elements thus removed the last doubt in my mind as to whether the "emanation substance" contains a new radio-active element (rare earth) different from radium. Thus it is not possible to impart artificially the characteristic power of emanation to inactive rare earths by contact with radium. If solutions of thorium, lanthanum, cerium, &c., to which radium has been added are precipitated with ammonia and washed, the precipitates are adulterated with traces of radium, and show, besides slight β -radiation, remarkably strong α -radiation, but yet no emanation similar to the emanation substance.

It has further appeared that all emanating substances which do not belong to the rare earths, such as the insoluble residue (*Berichte*, 1903, xxxvi., 343), which has not been further examined, the magnesium, strontium (and barium) precipitates lose their activity and power of emanation gradually, even if very slowly. These substances have originated secondarily by the influence of the emanation substance (by induction); unlike the rare earths they possess the maximum of activity and emanation immediately after separation; the gradual disappearance may require a year or longer.

We must not forget to notice that the complete removal of the emanation substance, especially in working with small quantities, as may be supposed, presents greater difficulties than that of radium. For example, with a magnesia preparation the activity was only very little diminished after one year. It may be assumed that the magnesia still contains traces of the emanation substance, even if no further precipitate is obtained with oxalic acid. It is just as difficult to free uranium oxide from the

* *Berichte*, 1903, xxxvi., 342.

† I have never been able to observe a discontinuous spectrum in self luminous radium bromide melted in glass tubes under ordinary pressure with air or hydrogen. The radium bromide in an atmosphere of hydrogen does not become brown as in air, but blue-black. The peculiar scintillating phosphorescence in this case is produced again by heating for a short time with desiccation; it often also is required without becoming fainter; probably because the altered bromide can be completely regenerated. See *Berichte*, 1902, xxxv., 3609.

emanation substance if it occurs as an adulteration of this substance, so that it does not retain a considerable activity. Uranium potassium sulphate prepared from it is strongly self-luminous. The small activity of the commercial uranium salts seems to me to depend rather on traces of the emanation substances than on radium if the uranium itself is inactive. The fact that in spite of previous repeated purification of the commercial uranium nitrate, the subsequent fractions exhibit not the same but different activity is in agreement with this theory.

Small quantities of lead, if they still adhere accidentally to the emanation substance and are afterwards separated by sulphuretted hydrogen, are very active, and remain so. I think that my former strongly active lead preparations (*Berichte*, 1902, xxxv., 102) have borrowed their activity from the emanation substance, especially as they were always found only in its immediate neighbourhood.

The feebly active lead salts of pitchblende (I have not yet been able to obtain the lead from pitchblende in a perfectly inactive state) which show an increase of activity, can also be infected by the most minute traces of radium.*

If an ordinary barium salt is added artificially to a solution of a feebly active rare earth and the barium is precipitated with sulphuric acid, the barium sulphate is more strongly active than the rare earth. By fractional crystallisation of the purified barium bromide the activity may be very quickly increased, just as in the case of the barium-radium mixture. The anhydrous salt phosphoresces strongly. Runge and Precht have compared the spark spectrum with equally active radium barium bromide. In the latter preparation the principal radium lines could be easily seen, but in the former they were not present. The most convenient method of distinguishing the two preparations is afforded by the immediate appearance of the maximum (β) activity, and by the power of emanation which may be shown by means of the zinc sulphide screen. Debieure (*Comptes Rendus*, cxxxi., 333) has previously obtained similar results by precipitation of barium sulphate from thorium-actinium solutions and crystallisation of the chloride. Unfortunately I have as yet had no opportunity of arranging comparative experiments with thorium from pitchblende and my lanthanum preparations, which would be of special importance in relation to the emanation.

The induced activity produced by the emanation in air is different as regards its disappearance from that in aqueous solution. Radium behaves similarly. But the inducing force is greater than in the case of the radium emanation, as I have specially noted before. Thus, for example, wadding, through which the emanation has been led for a short time, becomes as active as the substance itself; the disappearance only requires some hours. Goldstein (*Verh. d. Dtsch. Phys. Ges.*, November 13, 1903) has also recently observed the easy and rapid transposition of my emanation into induced activity. I have not been able to obtain an absorption (recognisable on the phosphorescence screen) by means of liquids.

I shall now endeavour—from the best lanthanum preparations thus accumulated—to isolate the new active rare earth. The effect of the preparations is very astonishing. It appears as a splendid phenomenon, visible to a great distance in a large lecture room, if a current of air is blown through tubes against a Sidot's blende screen of about $\frac{1}{4}$ sq. m. surface over the preparations, enclosed in paper capsules, and collected in a glass flask. The scintillation of the screen, which lasts for some time, is visible to the naked eye if the screen is held before the eye beyond the normal distance of sight. The sparks are clearer and larger respectively than with radium or polonium, hence a spintharoscope prepared with the emanation substance is far more effective. I have also been able to see the scintillation of ordinary glass in the flask in which it was kept (besides the uniform phosphorescence); but it appears much less striking than with Sidot's blende.

I shall for the future call the strongly radio-active

element, which is to be assumed as present in the emanation substance, and is presumably allied to lanthanum, "Emanium."—*Berichte der Deutsch. Chem. Ges.*, 1904, xxxvii., 1696.

COLORIMETRIC ESTIMATION OF CHROMIUM.

By A. MOULIN.

M. CAZENEUVE (*Bull. Soc. Chim.*, vol. xxix., p. 758) has already described the coloured reaction produced when diphenylcarbazide is brought into contact with chromic acid, or the chromates in general. A very intense purple-violet colour is thus produced; the reaction is extremely sensitive, and will show traces of chromium. As it only requires a relatively short time to acquire its final intensity, which then remains for some time, it seemed to us that it might very well be used for the rapid estimation of this metal.

Two solutions are necessary for this estimation:—(1) A solution of diphenylcarbazide; (2) A titrated solution of chromic acid.

1. *Solution of Diphenylcarbazide*.—The solution of diphenylcarbazide is prepared in the following manner:—

Diphenylcarbazide	..	..	..	2 grms.
Alcohol at 90°	..	..	..	100 c.c.
Acetic acid	..	..	..	10 "

Boil on the water-bath until completely dissolved, and make the volume up to 200 c.c. with alcohol at 90°.

2. *Chromic Solution*.—Weigh out 0.5 grm. of pure chromic acid, dissolve it in a little water, and make up the volume to 1000 c.c.; take 100 c.c. of this solution, place them in a graduated litre flask, and make up to 1000 c.c. with distilled water; thus we have a solution of which each c.c. represents 0.00005 of chromic acid, or 0.000026 of chromium.

We then weigh out 0.25 to 0.50 grm. of the sample to be examined, according to the supposed proportion of chromium present, dissolve it, and transform the chromium salt obtained into chromate by one of the ordinary methods.

With chrome-irons we obtained very good results by oxidising the salt of chromium, at boiling temperature, by peroxide of hydrogen in the presence of an excess of potash. This method of oxidation by peroxide of hydrogen has given us excellent results in every case.

When the oxidation is complete, we filter to separate the metals precipitated by the potash, wash the filter, and make the volume up to 100 c.c. or 200 c.c. according to circumstances, after having neutralised exactly with acetic acid. We then pour into graduated test glasses of 100 c.c. capacity, 2 c.c. of the diphenylcarbazide solution, and add about 70 c.c. of distilled water; into these test glasses we measured off 0.5 c.c., 1 c.c., 1.5 c.c., and 2 c.c., &c. of the titrated chromic solution, and into corresponding test glasses a known number of c.c. of the solution to be estimated; make up the volumes to 100 c.c., and after mixing leave them for twenty minutes for the reaction to become complete.

We then make the tints of the two series equal, and from this we can deduce the amount of chromium in the sample under examination.

This last operation can be simplified by the use of a Dubosq colorimeter.

This process, which we have often used, has given us very exact results, but it is essential, if the results are to be perfectly comparable, that the dilution of the chromate in the solution under examination should be as near as possible to that of the titrated solution because of the extreme sensitiveness of the reaction. It is also always preferable to add an excess of diphenylcarbazide solution; in fact, if the amount of the reagent used is insufficient the reaction becomes modified completely, and the general colour becomes more reddish, making the comparison with the scale difficult.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 6.

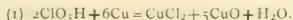
* Lead nitrate, for example, crystallises with barium radium nitrate.

THE ACTION OF COPPER ON CHLORIC ACID
WITH AND WITHOUT THE ASSISTANCE
OF ELECTROLYSIS.

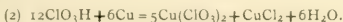
By ANDRÉ BROCHET.

CHLORIC acid attacks copper more or less energetically according to its concentration. With a solution containing 280 grms. of ClO_3H (density = 1.15) per litre, the attack at about $60-80^\circ$ is tumultuous; chlorised fumes are given off, but the reaction becomes quiet rapidly. At the ordinary temperature solution is rapid, the liquid becomes hot, but not hot enough for the reaction to become tumultuous. As the acid is diluted the attack becomes weaker. With normal acid (83.5 grms. per litre) solution is insignificant at the ordinary temperature (about 0.02 grm. per half hour or per hour).

Except in the case of gas being given off, which makes the action irregular, the latter may be represented by the equation—



The chloric acid in excess is rapidly saturated by the oxide of copper formed, so that the complete reaction is as follows:—



In the solution of the copper by chloric acid we observe that the ratio of the weight of the copper dissolved to the weight of chlorine passing from the state of chlorate to that of chloride, is about 5.36, as required by the reactions (1) and (2).

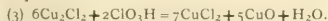
When all the acid is saturated the action of the copper continues on the chlorate thus formed.

In any case no evolution of hydrogen is observed, as has been noticed in the action of chloric acid on zinc or sodium amalgam (O. Dammer, "Handbuch der Anorganische Chemie"). If we electrolyse concentrated chloric acid at about $60-80^\circ$ with a copper anode, the attack will be naturally very rapid and tumultuous. It is also very rapid, but without the evolution of gas in the case of normal acid.

Under these conditions we also find 5.36 as the ratio of the copper dissolved to the chlorine in the form of chloride. The apparent reaction of the electrolyser thus corresponds to the reactions (1) and (2). The copper dissolved by the current, the same as the copper dissolved by chemical action, passes directly to the state of chloride and oxide; this latter remains in solution, thanks to the excess of chloric acid.

In electrolysis in the cold, principally with a normal solution, we observe that the copper becomes covered with a white deposit which has been identified as cuprous chloride; this deposit is not adherent, and the copper remains perfectly clean. When heated, the metal is brilliant, and there is no deposit of cuprous salt under these circumstances, which is incompatible with the excess of chloric acid.

Cuprous chloride, as I have been able to observe, reduces normal chloric acid fairly rapidly in the cold. If the chloride is in excess, there is a formation of complex basic salts; if the acid is in excess everything is dissolved. When hot the reaction is instantaneous; it is represented by the equation—



With concentrated acid, even in the cold, the action is complicated by the disengagement of oxidised compounds of chlorine. In the action of normal chloric acid on copper without using the electric current, the metal becomes covered with a yellow deposit of the cuprous hydrated oxide, which behaves in the same manner as the chloride, and gives a reaction analogous to (3). The action of chloric acid on copper, with or without electrolysis, such as is represented by the equations (1) and (2), is thus not

quite complete; it is, in fact, brought about, as we have just seen, by the intermediary of the cuprous compounds.

For these experiments I made use of the same apparatus as for those already published (*Bull. Soc. Chim.*, [3], vol. xxix., p. 156).

The apparatus consists of a porcelain paint-pot 500 c.c. in capacity. This kind of vessel has the drawback of not being transparent, though this is not of much consequence when heating on the water-bath; on the other hand, it has the advantage of being very solid and stable, thanks to the collar which enables us to put it directly into a ring on the water-bath; this is specially convenient with electrolytic operations where we often have to use systems of mechanical agitation connected with complicated apparatus. One of the electrodes is fixed to the pot and the other, generally the anode, to a stirrer worked by a hot-air motor.

The paint-pot is slightly conical, with an available height of 11 or 12 c.m., 7 c.m. diameter at the base, and 8 at the top, so that strips of metal 5 c.m. wide and 15 c.m. long can be used without danger of a short circuit, the available surface being 1 square decimetre. The amount of liquid used for each operation is 450 c.c. When a porous pot is required it should be 14.5 c.m. high and 4.5 c.m. diameter. In such a case we can have 200 c.c. in each compartment with a revolving electrode of 2.5 c.m. by 15 c.m. with an available surface of 50.2 square c.m.

My experiments, generally with a current of 4 ampères, were carried out on chloric acid, chlorate of potassium, and chlorate of copper acidulated with sulphuric acid. The chloric acid was obtained by mixing boiling solutions of chlorate of barium and sulphuric acid at 1 gm. molecule per litre, a slight excess of the former being used so as not to have free sulphuric acid in the final solution, which is about normal, after filtration. For the experiments with acid chlorate of potassium I used a solution containing 50 grms. of ClO_3K and 60 grms. of SO_4H_2 per litre.

The chlorate of copper was obtained by mixing two boiling solutions of chlorate of barium and sulphate of copper at 1 gm. molecule per litre, leaving a slight excess of sulphate of copper, and, after filtration and cooling, adding 60 grms. per litre of sulphuric acid.

These different liquids attack the copper in the same manner. Their action under the influence of electrolysis is the same. A platinum cathode was used in every case. The electromotive force, at first very low (0.2 to 0.3 volt), becomes gradually higher with chloric acid and chlorate of copper; with chlorate of potassium it remains practically constant.

In the case of the electrolysis of the acid solution of chlorate of copper, we notice at the commencement a deposit of copper on the cathode, but this soon disappears.

We may remark that in all these experiments the anode is attacked in a very regular manner instead of being perforated, as in the case of the electrolysis of chlorate of potassium.

Thus these different experiments show that copper, in the presence of chloric acid, is dissolved in the cuprous state, but that the salt thus formed changes more or less rapidly into cupric compounds under the influence of chloric acid in excess.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 6.

The Stolzenberg System of Keeping Notes.—The Stolzenberg system of filing documents was originally devised as a convenient adjunct to, or substitute for, the complicated system of book-keeping in vogue in many establishments. For some time past we have used the files and cabinets as a convenient means of storing notes of laboratory work and results in a form which renders them readily accessible when wanted; while additions in chronological order, or in that of subject-matter, can be inserted whenever desired. From experience we think that men of science and all engaged in original work will derive benefit from keeping their notes of researches in this systematic and convenient manner.

RADIO-ACTIVE MINERALS AND SUBSTANCES.

We have received the following communication from the United States Geological Survey:—

The United States Geological Survey is collecting information concerning the occurrence of radio-active minerals and substances in the United States, and would be pleased to have your co-operation. The minerals named on the appended list possess radio-active properties in various forms and degrees. Radio-activity has been noticed also in many substances which are not primarily minerals, such as slags, tailings from concentrators, slimes, chemical wastes, natural mineral waters, deep-well waters, and petroleum, and it is possible that the list of radio-active minerals and substances may be greatly increased. Anyone who has found such minerals or has observed radio-activity in any other substance is urged to give the Survey full details regarding the locality where those occurrences were noted. Any information which the Survey may be able to give will be cheerfully furnished.

The simplest means of detecting radio-activity in a substance is by the use of a photographic plate. The more sensitive the plate the better. The plate should not be removed from the enclosing black paper, and a metal object should be laid upon this black paper in a dark room; upon this should be placed the specimen to be tested. Instead of the metal object a few small nails may be arranged so as to form the initial of the owner and left on the paper-covered plate below the specimen. The specimen should be left in the dark room for from two to fifteen hours, and then developed in the usual manner. If the specimen has radio-active powers, a photograph of the metal object or of the nail-formed initial will be produced on the plate exactly as if it had been exposed to the sun's rays. The test should be made, if possible, with from half a pound to a pound of the material. The electrical method is more reliable, but is much more difficult.

Each specimen submitted should be plainly labelled with the name and post-office address of the sender, the name of the mine or claim from which it came, and the State, county, city, village, mountain, or district in which the deposit is located. If it is desired that the specimens be returned, it must be definitely so stated. On request the Survey will mail postal franks, which will enable the exhibitors to send free of postage a box of specimens weighing not more than four pounds. No specimens will be examined until the finder has first submitted a radio-graph made as described in the preceding paragraph.

Interesting specimens are especially desired for the Survey's exhibit at the Louisiana Purchase Exposition to be held in St. Louis, Mo., from April 30 to December 1 of the present year. This exhibit will be in the United States Government Building, and will be general and varied in character. It will include specimens of every known radio-active substance, whether obtained from minerals and ores, from mineral waters, or from petroleum wells. There will be shown also authentic specimens of radium compounds that have been made by noted investigators. Everything relating to the source, manufacture, and application of radium will be exhibited, including all chemicals obtained from the separation of various radium compounds, and all instruments and devices with which it is proposed to apply radio-activity in medicine, science, and the arts. An interesting feature will be the portraits and the publications of celebrated radium discoverers and investigators, together with photographs of their laboratories and apparatus, and autograph letters from some of them.

Two convenient halls will be set aside for demonstration of the properties of radium. In one will be grouped the specimens of ores and minerals containing radium, and careful note will be made of their effects upon various substances. In the other hall illustrated lectures will be given twice daily on a variety of subjects relating to the history, nature, and possibilities of radium. Its mode of occurrence,

the methods used in separating it from its ores, the concentration of activities from low to high, and the manifold uses to which these remarkable radio-active substances may be put will all be described. Cinematograph Hall will be so arranged that it can be easily darkened, and different highly active specimens of radium compounds will be exhibited in it as affecting the diamond, willemite, kunzite, and other radio-responsive substances.

Investigators of radium are cordially invited to notify the Survey of any material that they would like to exhibit or to put upon record. If they will kindly state the size and character of their material and the space needed for its display, every effort will be made to arrange for its immediate transportation and exhibition.

As the Exposition opened April 30, 1904, it is necessary that prompt action be taken concerning any specimens which are believed worthy of exhibit. All communications regarding the collection and examination of radio-active specimens by the Survey, and concerning its radium exhibit at St. Louis, should be addressed to Mr. George F. Kunz, No. 40, East 25th Street, New York.

CHAS. D. WACOTT, Director.

LIST OF MINERALS FOUND TO POSSESS RADIO-ACTIVE PROPERTIES.

Minerals containing Uranium.

Name.	Percentage of uranium oxide contained.	Radio-activity (Curie's list), uranium unit 1.	No. in Dana's Mineralogy.
Uranothallite	35-37	—	307
Liebigite	36-38	—	308
Voglite	37	—	309
Thorite	1-10	0.7-2	395
Var. Uranothorite ..	—	—	—
Rowlandite	0.04	—	—
Uranophane	53-67	—	503
Hatchettolite	15-16	—	521
Fergusonite	1-3	0.1-0.4	523
Var. Tyrilite	5-6	—	—
„ Bragite	8-9	—	—
Sipylite	3-4	0.1-0.3	524
Yttrotantalite	1-2	—	528
Samarskite	—	1.1	—
Var. —	9-16	—	529
Annerödite	16-17	—	530
Hielmitite	2-5	—	531
Euxenite	5-12	—	534
Polycrase	5-20	—	535
Arrhenite	23-24	—	535½
Xenotime	0-4	0.03	536
Torbernite	57-62	—	559
Zeunerite	55-56	—	660
Autunite	55-62	2.7	661
Uranospinitite	59-60	—	662
Uranocircite	56-57	—	663
Phosphuranylite ..	71-76	—	664
Trögerite	63-64	—	665
Walpurgite	20-21	—	666
Carnotite	62-65	—	—
Uraninite (pitchblende)	75-85	1.6-8.3	711
Var. Broggerite	—	Vary in ratio of uranium oxide.	—
„ Cleveite	—	—	—
„ Nivenite	—	1.4	—
„ Urannibolite	—	—	—
Gummite	61-75	—	712
Var. Thorogummite ..	—	—	—
„ Yttrogummite	—	—	—
Mackintoshite	21-22	—	—
Uranosphaerite	50-51	—	713
Johannite	67-68	—	806
Uranopilite	77-78	—	807

Minerals containing Thorium (continued).

(It has been pretty well established that thoria is not radioactive unless the mineral in which it is found contains uranium also).

Name	Percentage of thorium oxide contained.	Radio activity (Curie's list).
Tysonite	—	—
Fluocerite	—	—
Yttrocerite	—	—
Cassiterite	—	—
<i>Var.</i> Ainalite	—	—
Parisite	—	—
Bastnaesite	—	—
Lanthanite	—	—
Tengerite	—	—
Lavenite	—	—
W. hlerite	—	—
Eudialyte	—	—
<i>Var.</i> Euclolite	—	—
Cappelenite	—	—
Melanocerate	1-2	—
Caryocerite	13-14	—
Tritomite	8-9	—
Zircon	0-2	—
<i>Var.</i> Tachyaphalosite	Small amount	—
Cytrolite	trace	—
Thorite	48-72	0.7
<i>Var.</i> Auerlite	70	—
Calciothorite	50-60	—
Eucrasite	35-36	—
Freyalite	28-29	—
Orange	74-72	—
Uranothorite	52	2
Gadolinite	0-1	—
<i>Var.</i> Metagadolinite	—	—
Yttrialite	12	—
Thalénite	—	—
Allanite	—	—
<i>Var.</i> Bodenite	—	—
Muromonite	—	—
Orthite	—	—
Uralthorite	—	—
Cerite	—	—
Cenosite	—	—
Keilhauite	—	—
Tschermakite	0-21	—
Johnstrupite	—	—
Mosandrite	trace	—
Rinkite	—	—
Dysanalite	—	—
Pyrochlor	8	—
Hatchettolite	—	—
Microsite	—	—
Fergusonite	—	0.1-0.1
<i>Var.</i> Kochelite	1-2	—
Spyllite	—	0.1-0.3
Columbite (tantallite)	—	0.02
Tapiolite	—	—
Skogbolite	—	—
Stibiotantalite	—	—
Mossite	—	—
Yttrotantalite	—	—
Samaraskite	—	1.1
<i>Var.</i> From Colorado	3-4	—
Annerdite	2-3	—
Hielmité	—	—
Aeschynite	15-17	0.7
Polyminite	3-4	—
Zirkelite	7-8	—
Euxenite	0-6	—
Polycrase	3-4	—
Arrhenite	—	—
Rogersite	—	—
Xenotime	0-3	0.03
Monazite	0-18	0.5

Name	Percentage of thorium oxide contained.	Radio-activity (Curie's list), uranium unit t.
Rhabdophanite		
Churcinite		
Uraninite (Pitchblende) ..	0-10	1.6-2.4
Var. Broggerite	5-6	
" Cleveite	3-5	1.4
" Nivenite	6-8	—
" Urannibate		
Gummite	(0-42)	
Var. Thorogummite	41-42	
" Yttrogummite	0-3	
Mackintoshite	45-46	

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 18th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

BEFORE entering on the ordinary business of the meeting, the President said he thought it would be consonant with the wishes of the Fellows if he gave expression to the deep feeling of regret with which they had all received the news of the death of one of the most eminent of their past Presidents, Professor Williamson. A man of philosophic mind and great intellectual activity, he had been led in the later years of his life to abandon research in connection with chemistry in favour of other pursuits, hence it was difficult for chemists of the present generation to realise how great had been the influence exercised by his experimental researches and his writings on the progress of theoretical chemistry forty years ago. Williamson served the Society during many years on the Council, as vice-President, and for two separate periods as President. The Society had, of course, been represented at the funeral, at which many past and present officers of the Society—including himself and the Treasurer—had assembled, and a resolution of condolence with the family had that day been passed at the meeting of the Council.

Messrs. N. J. Bluman, J. C. Evans, G. Pinchbeck, and M. W. Stevens were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Harold Lowe, B.Sc., 59A, Fulham Park Gardens, S.W.; Henry Stanley Shelton, 4, Larden Road, Acton Vale, W.; Herbert Jenkins, 52, Criffel Avenue, Streatham Hill, S.W.; Rudolf Lessing, Ph.D., 33, Brunswick Square, W.C.; Robert Rodger, 54, Rostrevor Road, S.W.; William Edward Oakden, 2, Gledhow Terrace, South Kensington, S.W.; Charles John Sawyer, 6, Cleveland Road, Brighton.

A ballot for the election of Honorary and Foreign members was held, and the following were subsequently declared duly elected:—Prof. Antoine Henri Becquerel, Prof. Cornelis Adrian Lobry de Bruyn, Prof. Frank Wigglesworth Clarke, Madame Marie Curie, Prof. Carl Theodor Liebermann, Prof. Edward Williams Morley.

In reply to Prof. Divers, the PRESIDENT stated that Counsel's opinion had been taken on the question whether women were eligible for election as ordinary Fellows of the Society under the present Charter, and that the opinion was adverse.

*87. — *The Action of Nitrogen on the Human System.*
B. WILLIAM AUGUSTUS FULTON.

Pinene nitrosochloride having been shown by von Baeyer to have the double formula $(C_{10}H_{16}NOCl)_2$, it occurred to the author that the unsatisfactory yield of this compound by the usual processes might be improved by using a mixture

of equal quantities of *d*- and *l*-pinenes which is optically inactive. Whereas previously the yield of nitrosochloride from ordinary *d*-pinene was about 32 per cent of the pinene, and the product from the more highly rotatory pinene obtained from French turpentine was still less, the employment of a mixture prepared so as to be optically inactive gives 55 per cent.

The melting point of pure pinene nitrosochloride is not 103° , as originally given, but 115° (circa). Attempts to resolve pinyllamine into two optically active bases proved unsuccessful.

For the regeneration of pinene from the nitrosochloride, methylaniline is recommended in preference to aniline, as there is no violent action and the yield of pinene is great.

Finally, it is shown that when the nitrosochloride is converted into nitrosocyanide (Tilden and Burrows, *Proc.*, 1902, xviii., 161) or into the piperidylnitrolamine, the compound becomes monomolecular at the same time that the nitroso-group assumes the *isonitroso*- or oxine structure.

DISCUSSION.

Professor MELDOLA suggested that the base produced by the action of dimethylaniline on pinene nitrosochloride might be Bindschedler's green resulting from the secondary interaction between nitrosodimethylaniline and the excess of dimethylaniline present under the conditions of the experiment (*Ber.*, 1883, xvi., 864).

*88. "The Electrolytic Estimation of Minute Quantities of Arsenic." By HENRY JULIUS SALMON SAND and JOHN EDWARD HACKFORD.

A high supertension of the cathode is requisite for the reduction of arsenic acid to metallic arsenic, the reaction being most readily effected in the presence of metals having this property, such as lead or zinc and probably also mercury. Platinum, having a low supertension, is quite inefficient.

The production of arsenic trihydride from arsenites is accomplished more readily by platinum cathodes than by those of copper, which have a much higher supertension. In this case, mercury, with an extremely high supertension, is quite unsuitable. A certain amount of supertension, however, appears to be necessary, for platinised platinum with no supertension is inefficient.

The authors recommend the use of lead electrodes for the estimation of minute quantities of arsenic, as their application causes a simplification of previous methods. Errors which may arise in the electrolytic methods owing to the presence of foreign metals can be rectified by the addition of lead acetate or zinc sulphate to the electrolyte except when the foreign metal is mercury. When lead and zinc cathodes are used, the smallest amount of arsenic which can be detected in alkaline solutions of arsenates and arsenites is about thirty times as great as in acid solution, but platinum cathodes are quite unsuitable.

DISCUSSION.

Dr. F. M. PERKIN remarked that although the electrolytic apparatus gave good results even with very minute quantities of arsenic, it was, however, a great advantage to have an apparatus in which lead was employed for the cathode instead of the very expensive platinum. The fact that a mercury cathode did not give good results, although there was considerable over-voltage, was due to the formation of an arsenic amalgam, which then escaped the reducing action of the hydrogen. An aluminium cathode is suitable for dilute sulphuric acid solutions, because in this case there is considerable over-voltage and the metal is very slightly attacked, and is, moreover, free from arsenic.

Had nickel electrodes been tried in an alkaline solution? The only drawback to the electrolytic method for detecting arsenic is the trouble of preparing the mirrors, especially when special standards are made for each substance tested.

Dr. STEVENSON asked what was the authors' evidence

that the lead of commerce can be obtained free from arsenic.

Mr. SAND, in reply, said the electrolytic experiments in alkaline solutions had not been found satisfactory, and had, moreover, not been tried in the case of nickel.

The preparation of mirrors for each kind of material examined was not absolutely necessary, but, nevertheless, this precaution rendered the comparisons more certain.

Several grms. of commercial lead had been examined for arsenic with a negative result. The lead most frequently used for cathodes was purest assay lead, whereas pure commercial lead was employed for anodes. New electrodes often contain a small amount of arsenic on the surface, but in all cases they were tested by blank experiments.

*89. "The Action of Sodium Methoxide and its Homologues on Benzophenone Chloride and Benzylidene Chloride." Part II. By JOHN EDWIN MACKENZIE and ALFRED FRANCIS JOSEPH.

The authors have found that benzhydrol is formed in the preparation of diisopropoxy-, diisobutoxy-, and diisoamyloxy-diphenylmethanes by the action of the respective sodium alkoxides on benzophenone chloride (compare *Trans.*, 1901, lxxix., 1204). It is also shown that dibenzoyldiphenylmethane, like its homologues, readily splits up into benzophenone and dibenzyl oxide.

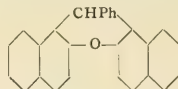
The anhydride of phenyl-β-hydroxynaphthylmethane has been obtained by the action of benzylidene chloride on β-naphthol, and found to agree in properties with the substance prepared by Claisen (*Annalen*, 1887, ccxxxvii., 261) from benzaldehyde and β-naphthol. This product was also obtained when the reaction was carried out in xylene solution and when sodium naphthoxide was used instead of naphthol. Claisen's dihydroxy-compound could not be isolated.

Nitration experiments on the anhydride led to the formation of substances containing from two to six nitro-groups.

When treated with fuming sulphuric acid, the anhydride yielded a β-naphtholdisulphonic acid, but concentrated sulphuric acid gave rise to a product dissolving in water to a bright red solution, the colour of which was destroyed by alkalis and restored by acids.

DISCUSSION.

Professor MELDOLA said that in his opinion the constitution of Claisen's compound might be more correctly represented by the following formula:—



as it was more in harmony with the general properties of β-naphthol that the *α*-ortho-position, and not the second β-position, should be first attacked.

Dr. HEWITT stated that the hydroxylic compound, $C_6H_5 \cdot CH(C_6H_5 \cdot OH)_2$, is easily produced by condensing benzaldehyde and β-naphthol in cold acetic acid solution by the aid of hydrochloric acid, and from this the anhydrous substance can be obtained in good yield by heating with acetic acid in sealed tubes.

The colouration observed on dissolving the anhydride in strong sulphuric acid is probably due to oxidation and formation of a carboxonion salt similar to those already studied by Werner, Fosse, and himself.

Dr. MACKENZIE replied that at present he had no decided views in favour of the 2:3-structure of the anhydride molecule as against the 1:2-configuration; he had not yet obtained any substitution products in support of either of these constitutions.

*90. "The Bromination of Phenolic Compounds." By JOHN THEODORE HEWITT, JAMES KENNER, and HARRY SILK.

When one molecular proportion of bromine acts on phenol, the character and proportions of the products obtained vary with the conditions under which the reaction is carried out. In aqueous solution, the phenol is apparently not all brominated, some of the bromine being used in forming higher substitution products. Absence of water and presence of a strong mineral acid favours the formation of *p*-bromophenol; the quantity of the para-compound diminishes, however, if sodium acetate is added to a glacial acetic acid solution of phenol before bromination, but is slightly increased by the addition of concentrated sulphuric acid.

If more than one molecular proportion of bromine is added to a solution of phenol in concentrated sulphuric and glacial acetic acids, the second molecule of bromine is utilised very slowly, the sulphuric acid hindering substitution in the ortho-position, but by brominating phenol in excess of 73 per cent sulphuric acid, the halogen rapidly enters into reaction, and a nearly quantitative yield of 2:4-dibromophenol is obtained, apparently without any admixture of tribromophenol.

5-Bromosalicylic acid can be conveniently prepared by brominating salicylic acid in a mixture of sulphuric and acetic acids.

4-Bromo-*a*-naphthol cannot, however, be obtained from *a*-naphthol under similar conditions, dibromination taking place.

DISCUSSION.

Professor MELDOLA pointed out that in the case of the naphthols it was well known that the first action of bromine is to produce additive products from which hydrogen bromide is expelled by heat. With reference to the influence of temperature as determining the formation of *o*-bromophenol instead of the para-compound, he called attention to Merck's German patent (No. 76,597, of 1893), in which it is claimed that by chlorinating or brominating phenol at 150°–180° the corresponding halogenated ortho-derivative is produced.

91. "The Decomposition of the Alkylureas." (Preliminary Note.) By CHARLES EDWARD FAWSITT.

The author has already shown (*Zeit. physikal. Chem.*, 1902, xli., 601) that the decomposition of urea by acids is not a case of ordinary hydrolysis, but is the result of a secondary decomposition, following an isomeric transformation into ammonium cyanate. An investigation of the velocity of decomposition of the alkylureas with acids by similar methods shows an exact parallel with the case of urea. The hydrolysis is indirect, and is effected as a secondary reaction of the acid with the alkylammonium cyanate. Methylurea is decomposed more slowly than urea, but dimethylurea much more rapidly.

*92. "The Formation of Periodides in Nitrobenzene Solution. Part II. Periodides of the Alkali and Alkaline Earth Metals." By HARRY MEDFORTH DAWSON and ETHEL ELIZABETH GOODRY.

Previous experiments relating to the nature of the periodides which are formed in nitrobenzene solutions containing iodine and potassium iodide (Dawson and Gawler, *Trans.*, 1902, lxxxi., 524) have been extended to the iodides of the other alkali metals, and to those of the alkaline earth metals, and ammonium and substituted ammoniums. In general, these iodides have properties similar to those of the potassium derivative, and the experimental data indicate that enneiodides of the type $M'I_9$ or $M''I_8$, which are the essential components of such solutions when saturated with iodine, probably represent the highest limiting type of periodide, for the solvent used in these experiments appears to be specially suited to the formation of such periodides, and saturation of the solution with iodine favours the formation of the most complex product.

In the case of certain substituted ammonium radicles, enneiodides have been already isolated, and the analogous behaviour of the alkali and alkaline earth metals indicates

the possibility of preparing enneiodides of these metals under favourable conditions.

Periodides are also formed by the bromides of the alkali metals in nitrobenzene solution and to a small extent by the chlorides.

Compounds of lithium iodide with nitrobenzene and *o*-nitrotoluene, and of sodium penta-iodide with nitrobenzene have been isolated.

93. "The Action of Ozone on Ethane." (Preliminary Note.) By WILLIAM ARTHUR BONE and JULIEN DRUGMAN.

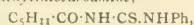
The authors have obtained ethyl alcohol by the interaction of ethane and ozone at 100°. Two experiments have been carried out as follows:—Ethane and ozonised air (O_3 = about 24 per cent) were separately led into the top of a vertical, wide glass tube, about 18 inches long, packed with glass beads and heated by a steam jacket. The proportions of the gases were so regulated that the ethane was always present in large excess, under which conditions the ozone entirely disappeared as the mixture slowly descended the tube. The gases were then drawn through a series of cooled glass worms containing water for the absorption of soluble intermediate products. Each experiment extended over three or four days, during which about 5 litres of ethane and 13 to 15 litres of the ozonised air passed through the apparatus. Subsequent examination of the liquid from the coolers showed that it contained ethyl alcohol, acetaldehyde, and traces of formaldehyde. The presence of ethyl alcohol was proved by first oxidising the aldehydes by means of an excess of an ammoniacal silver solution at the ordinary temperature (one hour), then acidifying the liquid with dilute sulphuric acid and submitting it to distillation in steam. The distillate in each case at once gave the iodoform reaction; the precipitate was composed of microscopic crystals, which slowly formed the characteristic star-like aggregates. As a precaution, the absence of acetaldehyde from the distillate was proved by the negative result obtained with Schiff's reagent. An examination of the gaseous products showed that they did not contain acetylene, ethylene, or free hydrogen.

There can be but little doubt, therefore, that ethyl alcohol is the primary product in the slow combustion of ethane. At temperatures where ethane begins to react with oxygen with appreciable velocity, the alcohol is oxidised so many times faster that it is practically impossible actually to detect its formation (compare Bone and Stockings, *Proc.*, xx., p. 106). The authors propose to continue the experiments, and to extend them to ethylene, acetylene, and other typical hydrocarbons.

94. "Caproylthiocarbimide." By AUGUSTUS EDWARD DIXON.

Caproyl chloride, dissolved in benzene, interacts spontaneously with finely-powdered ammonium thiocyanate, yielding caproylthiocarbimide, $C_5H_{11}CO \cdot NCS$; b. p. 108°/23 mm.; sp. gr. = 1.0165 at 18°/15°. This liquid is slowly hydrolysed by boiling water into caproic and thiocyanic acids; when heated with an alkaline lead salt, it yields metallic sulphide, together with thiocyanate, and is readily desulphurised by ammoniacal silver nitrate. If brought into contact with primary and secondary amines, direct union occurs, with formation of the corresponding thiocarbamides.

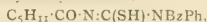
ab-Caproylphenylthiocarbimide,—



separates from alcohol in felted masses of needles, melting at 77°–78° without decomposition; when dissolved in hot dilute caustic alkali, the caproyl group is removed, leaving phenylthiourea.

ab-Caproyl-*o*-tolylthiocarbimide melts at 97°–98° and generally resembles the phenyl compound. When treated in hot alcoholic solution with the calculated quantity of silver nitrate, it yields the corresponding ab-caproyl-*o*-tolylurea (m. p. 99–100). ab-Caproyl-*p*-tolylthiocarb-

amide (m. p. 90—91°), when treated with silver nitrate, yields caproyl-p-tolylurea, melting at 131—132° (corr.).
n-Caproylphenylbenzylthiourea,—



was obtained from benzylaniline and the thiocarbimide; it separated from alcohol in vitreous prisms melting at 77—78°, and was not affected by boiling with neutral or ammoniacal silver nitrate; when boiled with caustic alkali, the caproyl group is eliminated, leaving a residue which can be desulphurised by an alkaline solution of lead.

Since, by interaction with water, the parent oil gives thiocyanic acid instead of carbon oxysulphide, its behaviour in these circumstances must be accounted that of a thiocyanate; on the other hand, the power to combine with nitrogenous bases, thereby yielding substituted thiocarbamides, places it among the isothiocyanates. This dual capacity is in accordance with the view developed in earlier papers by the author (*Trans.*, 1901, lxxix., 542; 1904, p. 350), that a variety of tautomerism subsists amongst the thiocyanates of electronegative radicles, the characteristic sulphuretted group of which may act either as $\cdot\text{SCN}$ or $\cdot\text{NCS}$. Moreover, in certain cases, both forms appear to be simultaneously active (Doran, *Proc.*, 1904, xx., 20), the preponderance of one or other depending almost entirely on the temperature at which interaction is caused to take place.

NOTICES OF BOOKS

A Text-book of Ceramic Calculations. With Examples. By W. JACKSON, A.R.C.S. London, New York, and Bombay: Longmans, Green, and Co. 1904. Pp. 67.

This book has been written primarily for the use of the classes in pottery and porcelain manufacture, held under the direction of the Staffordshire Education Committee. It contains a good deal of practical as well as theoretical instruction on compounding mixtures of known composition, the application of such methods to the complete synthesis of mixtures, &c., and the general subject of pottery making. The rational analysis of clay, and the application of this method to the synthesis of bodies are also dealt with in two chapters. There is a complete list of elements, compounds, and minerals of importance in pottery manufacture, with their formulæ, composition, &c., but there is no index.

Report on the Agricultural Work in the Botanic Gardens and the Government Laboratory at British Guiana for the Year 1902-1903. Georgetown, Demerara: C. K. Jardine, Printer to the Government.

THE bulk of this report consists of tables of results obtained from the experiments on the effect of various manures on sugar-cane growing. The general deductions as to the action of these manures are that nitrogen in the form of sulphate of ammonia, nitrate of soda, &c., is without doubt the manurial constituent, the supply of which mainly governs the yield of the plant; on the whole the former is the preferable salt to employ, and dressings of 2 to 3 cwt. of sulphate of ammonia per acre appear to be the most certainly profitable applications of nitrogen, though in favourable seasons the use of still higher proportions may prove successful; we may remark, however, that it is not until the season is over that it can be known whether it has been a favourable one or not, so how is the planter to know when he is to apply the larger amount of sulphate of ammonia? The application of superphosphate of lime in addition to manurings of nitrogen and potash is found to be advantageous with plant-canes only, ratoons should be manured with nitrogen only. The use of lime has resulted in largely increased yields, but whether or not its use is

profitable depends on the price of sugar; it is, however, confirmed that neither the addition of phosphoric acid, potash, or lime to the manures favourably affects the sugar contents of the juice.

Dictionary of Photographic Chemistry. ("Dictionnaire de Chemie Photographique"). For the Use of Amateurs and Professionals. By G. and AD. BRAUN fils. In Eight Monthly Parts. Paris: Gauthier-Villars. 1904. Pp. 500. Parts I., II., and III.

THIS dictionary comprises the nomenclature and description of all substances connected with photographic science. After a short general account of each preparation, the authors give its various chemical properties, and lay special stress on any of its applications to photography. All the photographic reactions as well as the most important manipulations are fully described, preference being given to practical operations rather than to theoretical discussions. This dictionary will be of great use to those engaged in photography, either as professionals or as amateurs, who really wish to understand what they are doing, as opposed to merely "pushing the button."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature in Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 18, May 2, 1904.

Electrolytic Solution of Platinum. New Method for Preparing Platinocyanides.—André Brochet.—Platinum behaves in the same way as iron and cobalt towards an alternating current, and dissolves very easily in cyanides. This fact is especially interesting, because this metal offers so much resistance to chemical agents. The explanation of this solution is particularly instructive from a theoretical point of view, and the author is further investigating the matter.

Origin of the Blondlot Rays emitted during Chemical Reactions.—Albert Colson.—Chemical actions which emit Blondlot rays are always accompanied by physical actions (contraction, cooling, &c.) which act in the same sense. Also as certain brisk reactions—such as precipitation of salts, oxides, &c.,—emit no N or N₂ radiation, apparently there exists no definite relationship between the intensity of the chemical reactions and the emission of these rays. It is just this want of proportion which renders the Blondlot rays of use to the chemist to disclose secondary or delicate reactions, often masked by the brisk reaction.

Reduction of Silicon by Hydrogen.—A. Dufour.—Silicon is reduced at a high temperature by hydrogen, producing silicuretted hydrogen and water. The reverse reaction is possible. This reduction explains the phenomenon of the apparent devitrification of silicon bulbs when they are blown by tubes. This reaction also gives a satisfactory explanation of Boussingault's and Schützenberger's experiments on silicification of platinum by silicon in an atmosphere of hydrogen.

Zinc-aluminium Alloys.—Hector Picheux.—The author tries to unite zinc and aluminium in all proportions, and he succeeds in isolating nine fairly definite alloys, corresponding to the following formulæ:—Zn₃Al, Zn₂Al, ZnAl, ZnAl₂, ZnAl₃, ZnAl₄, ZnAl₅, ZnAl₆, ZnAl₁₀, and ZnAl₁₂. He melts these in cylindrical ingots of 1 c.m. diameter, and in spheres 2.70 m.m. diameter. The fusion of these alloys presents an interesting peculiarity, which explains the great heat of fusion of zinc, 28.13°. When solid zinc

is thrown into melted aluminium (650°), the zinc being at the ordinary temperature, the latter melts slightly in contact with the aluminium, then all the aluminium solidifies. The mixture has then to be re-heated to obtain the fusion of the two metals, which afterwards mix intimately.

Action of Diazobenzene Chloride on Diphenylamine.—L. Vignon and A. Simonet. The body obtained by the action of diazobenzene chloride on diphenylamine has the constitution of phenyldiazamidobenzene, $C_6H_5 \cdot N=N \cdot C_6H_5 \cdot N_2$. The method employed for its preparation can apparently be used for the preparation of a series of new diazamide bodies, derivatives of diphenylamine and analogous bases.

Allyl- and Propenylalcoyketones.—L. E. Blaise. The author makes a series of researches to absolutely define the constitution of the non-saturated isomeric ketones, some being propenyl and the others allyl.

Application of Grignard's Reaction to the Halogen Ethers of the Tertiary Alcohols.—L. Bouveault. The author succeeds in applying Grignard's reaction to the tertiary chlorides of butyl and amyl, but he establishes the fact that the organo-magnesium derivatives thus obtained only partially obey Grignard's rules.

Symmetric Bichlormethyl Oxide.—Marcel Descudé. Symmetric bichlormethyl oxide can be obtained by the action of chlorine ether on methyl oxide or on monochlormethyl oxide. The author showed in a previous research that it is produced as a secondary product by the general action of acid chlorides on polyoxymethylene in presence of zinc chloride. He now further discovers that it can be obtained as the principal product of the reaction of phosphorus trichloride and $(CH_2O)_n$.

MISCELLANEOUS.

Technological and Scientific Dictionary.—We have received from the publishers, Messrs. George Newnes, Limited, a copy of Part II. of the new "Technological and Scientific Dictionary" they are now bringing out. This number comprises those subjects between BOW (Bow Compasses) and C O F (Copper Glance). The Dictionary contains in addition to many special articles, definitions of the terms used in all the principal scientific and technological subjects, and when complete should form a useful addition to the reference library.

The Carbonatopentamine Cobaltic Salts.—A. Werner and N. Goslings. These salts, which answer to the general formula $CO_3Co(NH_3)_5X$, are very soluble and of a brown to violet-red colour; they have only a single one of the carbonate reactions; that is, they give off carbonic acid with acids. *The Nitrate.* $CO_3Co(NH_3)_5NO_3 \cdot H_2O$.—We mix a solution of 100 grms. $(NO_3)_2Co$ in 50 c.c. of water, with a solution of 150 grms. of carbonate of ammonium in 150 c.c. of water and 250 c.c. of ammonia at $20^{\circ}5'$; expose to the air for twelve hours at the ordinary temperature. Sixty-eight grms. of pointed red crystalline tufts and plates are then deposited; we can re-crystallise these in warm water as bright brownish-red plates. This salt can be obtained in a more pure form by the reaction of NO_3Ag on the corresponding iodide; after the separation of the AgI, we add alcohol. Red plates are formed which are washed with alcohol and ether, and which are re-crystallised in water on the water-bath. With dilute acids CO_2 is given off. Iodomercurate of potassium gives a precipitate; the ferro- and ferricyanides give a brown precipitate, and after some time $PtCl_6Na_2$ gives a yellow precipitate, and $S_2O_6Na_2$ gives a crystalline red one. *The Bromide.* $CO_3Co(NH_3)_5Br \cdot H_2O$. The nitrate is dissolved in a very small quantity of water, and solid KBr added; on the addition of alcohol a brownish-red crystalline precipitate is formed which, when taken up with tepid water, gives large, red, quadratic crystals, very soluble in water, decom-

posing above 80° . *The Iodide.* $CO_3Co(NH_3)_5I \cdot H_2O$. This salt is prepared in the same manner as the bromide: it is a deep red crystalline powder, and after re-crystallisation in water, it forms very soluble red tables. —*Brichte*, *Chem. Ber.*, p. 2478.

Compounds of Nitrate of Silver with Ammonia.—V. Kourilof.—The author only gives the results of his researches, which are as follows:—1. Reyher's mono-ammoniacal compound, $AgNO_3 \cdot NH_3$, cannot be formed from aqueous or alcoholic solutions of ammonia and nitrate of silver, except when we take very accurately determined proportions of the two constituents. 2. The influence on the composition of Reyher's compound of small variations in the concentration of the nitrate of silver and the ammonia, and the impossibility of crystallising it in alcohol, show that it is a crystalline mixture of $AgNO_3 \cdot 2NH_3$ and of $AgNO_3$. 3. The separation of this crystalline mixture from its alcoholic solutions by the addition of ether, results from the slight solubility of $AgNO_3 \cdot 2NH_3$ and of $AgNO_3$. 4. We know that the solubility of $AgNO_3$ in alcohol diminishes with the proportion of water present; the saturated solution of $AgNO_3$ in anhydrous alcohol (density = 0.7993 at 15° C.) contains at $22^{\circ}9'$ 0.1754, and at $23^{\circ}3'$ 0.1804 molecules per litre. 5. The addition of 2 molecules of ammonia to the saturated solution of nitrate of silver makes the solubility four to six times less (at $22^{\circ}9'$ the solubility of $AgNO_3 \cdot 2NH_3$ is 0.0383 molecule). 6. The solubility of $AgNO_3 \cdot 2NH_3$ in alcohol increases slowly with the temperature; between 19° and 50° it is represented by an almost straight line (at 19° , 0.0353 molecule; at 30° , 0.0495 molecule). 7. The isotherms of the variation of solubility of $AgNO_3 \cdot 2NH_3$ in alcohol, for variable quantities of NH_3 , has a characteristic peculiarity; the solubility of $AgNO_3 \cdot 2NH_3$ increases at first with the proportion of NH_3 , reaches a maximum, then diminishes. 8. Between -14° and $+40^{\circ}$, aqueous or alcoholic solutions of nitrate of silver saturated with ammonia, do not separate any other ammoniacal compound than $AgNO_3 \cdot 2NH_3$. —*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 843.

MEETINGS FOR THE WEEK.

- MONDAY, 6th.—Royal Institution, 5. General Monthly Meeting.
Society of Chemical Industry, 8. "Loss and Nitrate in the Chamber Process," by J. K. H. Innes. "Acetone: its Manufacture and Purification," by A. Marshall. "New Method for the Estimation of Tannin," by Dr. J. Gordon Parker and E. B. M. Payne.
THURSDAY, 9th.—Faraday Society, 8. "The Hard and Soft State in Metals," by G. T. Beilby. "The Electric Furnace—its Origin, Transformation, and Applications," by Adolphe Minet.

TO CORRESPONDENTS.

J. T. Lewis.—The results you describe are likely to have a commercial value, but it is impossible to say more unless a trial is made on large quantities of tar and petroleum.

THE SIR JOHN CASS TECHNICAL INSTITUTE.

LECTURE ASSISTANT required for the CHEMISTRY DEPARTMENT, to act as a Laboratory Assistant, Salary 25s. to 30s. per week, according to qualifications. Applications, stating experience and qualifications, to be sent to the undersigned by SATURDAY, JUNE 11th.

CHARLES A. KOTIN, Principal.

31, Jewry Street, Aldgate, E. C.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC. As described in the "Report of the Inland Revenue Departmental Committee on Arsenic Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, &c.

UNIVERSITY COLLEGE of SOUTH WALES and MONMOUTHSHIRE, Cardiff.

The Council of the College invite applications for the following Posts:—

1. ASSISTANT LECTURER in MATHEMATICS.
2. DEMONSTRATOR and ASSISTANT LECTURER in CHEMISTRY.
3. DEMONSTRATOR and ASSISTANT LECTURER in PHYSICS.
4. DEMONSTRATOR and ASSISTANT LECTURER in PHYSIOLOGY.
5. DEMONSTRATOR and ASSISTANT LECTURER in BOTANY.

In the case of the appointment in Physics, preference will be given to candidates who have some knowledge of the technical applications of Electrical Science.

Further particulars may be obtained from the undersigned, to whom applications, with testimonials (which need not be printed), must be sent, endorsed on the outside with the title of the Department in which the application is made, on or before MONDAY, JUNE 20th, 1904.

J. AUSTIN JENKINS, B.A.,

Registrar.

University College, Cardiff,
May 16, 1904.

E. GEORGE & SONS, BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.,

Are OPEN to PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1850, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.

THE CHEMICAL NEWS AND JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 10 words to line)	0	3	6
Each additional line	..	..	0 6
Whole column	..	..	1 5 0
Whole page	..	..	3 0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.
LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.

RADIUM

ON SALE AND LET ON HIRE.—Write for terms.

The following can be had by return of post.

Pitchblende, direct from Joachimsthal, very radio-active, from 1/- to 30/- per piece.

Itacolomite, or flexible sandstone, 10/- to 25/- per piece (very rare).

Kunzeite, 1/- per gramme. Selected, clear, 2/-

Spartelite (see NATURE, 31/3/04, fol. 523), 2/- and upwards.

Chlorophane, 2/- and upwards Barium Platino Cyanide in large Crystals in course of manufacture. (ORDERS BOOKED).

Zinc Sulphide. Phosphorescing a beautiful Green, 2/8 per tube.

Calcium Sulphide " " Yellow, 2/6 "

Radio-active Residue from which Radium is made; very scarce, 2/ tube.

Polonium Sulphide, in tubes of one gramme, 21/-

" on Bismuth Rod or Disc, ... 25/-

" on Copper " " 25/-

Radio-active Screens (Willemite), 6d. per sq. inch. Plat. Bar.

" " (Zinc Sulph.), 10 x 10 cm. 7/6.

Professional Men, Universities, Schools, &c., allowed special terms

Our newly invented Thorium Inhalers may be had on hire.

ARMBRECHT, NELSON & CO., 71 & 73 DUKE ST., GROSVENOR SQ., LONDON, W.

Telephone: GERRARD 4942.

N.B.—We have to-day received a consignment of the New Zealand Vegetable Caterpillar; it is from 2 to 3 inches long, with a stem showing fructification growing out of its head. Scientific name of the insect is *Hepialus virescens*; the name of the fungus is *Sphaeria Robertiana*. Specimens may be had from 10/6 to 21/-, according to quality and size.

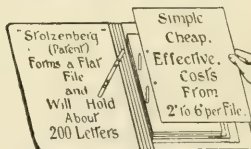
TERMS CASH WITH ORDER.

Goods may be returned if not approved of, when money will be refunded.

Perfect Order amongst your Scientific Papers, Research Records, &c.,

IS SECURED BY THE

"STOLZENBERG" SYSTEM OF FILING.



The "Unit" of the System is a simple flat File, made in six distinct colours, for classifying under Subjects, &c.

Used by SIR WILLIAM CROOKES, LORD KELVIN, Royal Commission on Tuberculosis, Baden Aniline Works (50,000), and by thousands of private persons as well as Business Concerns.

Satisfaction guaranteed; otherwise goods taken back and money returned.

Sample Set, consisting of 12 best Files, 4to and fcap., with strong nickel-plated Perforator, and Patent Lifter, packed in leather-board box, 10/6 post free.

THE STOLZENBERG PATENT FILE CO.,
50, Bishopsgate St. Without, London, E.C.

THE CHEMICAL NEWS.

Vol. LXXXIX., No. 2324.

PREPARATION OF SAMARIA AND ATOMIC WEIGHT OF SAMARIUM.

By G. URBAIN and H. LACOMBE.

DEMARÇAY has already prepared and described pure samaria (*Comptes Rendus*, cxxx., 1185). He has also satisfied himself that no intermediate element exists between neodymium and samarium. Further, he found that pure samarium gives more variation in the absorption than in the spark spectrum.

However, in his method there are eight to ten fractions between the samarium and the europium, and he could scarcely affirm on this evidence that no unknown earth exists between these two elements, the very characteristics of europium being of such a nature as to warrant its being of a complex nature.

We mentioned the principle of our method in a preceding communication (*Comptes Rendus*, cxxxviii., 792; cxxxviii., 84; *CHEMICAL NEWS*, lxxxviii., 295; lxxxix., 52); and, on further development of this, we have been able to actually separate completely from a mixture of rare earths pure samarium oxide.

been explained in our previous communication on europium. Particularly, we have allowed for the presence of free sulphuric acid in our sulphates, and so we have precipitated and washed with alcohol before crystallising from water until the aqueous solution is absolutely neutral to litmus.

On the other hand, the consecutive estimations of water are controlled by the sulphuric acid, and if the crystals only contain octohydrates we can obtain between the calculated atomic weights—either by the estimation of water, or by the estimation of sulphuric anhydride—a remarkable concordance, which is shown by the following measurements:—

	First measure- ment.	Second measure- ment.	Third measure- ment.	Mean
Hydrated sulphate ..	2'5107	3'2200	2'8382	
Anhydrous sulphate ..	2'0172	2'5872	2'2804	
Oxide	1'1918	1'5344	1'3508	
H ₂ O, per cent	19'655	19'652	19'653	
SO ₃ , per cent	32'755	32'757	32'753	
Sa ₂ O ₃ , per cent	47'588	47'590	47'593	

Atomic weight deduced from the transforma- tion of—

Sa ₂ (SO ₄) ₃ +8H ₂ O into				
Sa ₂ (SO ₄) ₃	150'30	150'37	150'35	150'340
Sa ₂ (SO ₄) ₃ into Sa ₂ O ₃ ..	150'34	150'33	150'37	150'346
Sa ₂ (SO ₄) ₃ +8H ₂ O into				
Sa ₂ O ₃	150'33	150'34	150'37	150'346

Samarium extracted from gadolinite.

	Heads.	Middle.	Tails.
Hydrated sulphate (grms.) ..	1'0499	1'2898	1'3650
Anhydrous sulphate (grms.) ..	0'8435	1'0362	1'0969
Oxide (grms.)	0'4996	0'6137	0'6497
H ₂ O, per cent	19'655	19'661	19'641
SO ₃ , per cent	32'755	32'757	32'761
Sa ₂ O ₃ , per cent	47'585	47'597	47'597

Atomic weight deduced from the transformation of—

Sa ₂ (SO ₄) ₃ +8H ₂ O into Sa ₂ (SO ₄) ₃	150'24	150'19	150'58
Sa ₂ (SO ₄) ₃ into Sa ₂ O ₃	150'33	150'30	150'34
Sa ₂ (SO ₄) ₃ +8H ₂ O into Sa ₂ O ₃ ..	150'31	150'28	150'13

Samarium extracted from earths rich in yttria (monazite sands).

	Heads.	Middle.	Tails.
Hydrated sulphate (grms.) ..	1'7992	1'8636	0'8407
Anhydrous sulphate (grms.) ..	1'4453	1'4977	0'6749
Oxide (grms.)	0'8557	0'8873	0'4001
H ₂ O, per cent	19'669	19'634	19'721
SO ₃ , per cent	32'770	32'753	32'687
Sa ₂ O ₃ , per cent	47'560	47'612	47'591

Samarium extracted from our first material containing europium.

	Heads.	Middle.	Tails.
Hydrated sulphate (grms.) ..	2'5107	3'1171	2'9425
Anhydrous sulphate (grms.) ..	2'0172	2'5045	2'3635
Oxide (grms.)	1'1948	1'4840	1'4004
H ₂ O, per cent	19'655	19'652	19'677
SO ₃ , per cent	32'755	32'738	32'730
Sa ₂ O ₃ , per cent	47'588	47'608	47'592

By several similar treatments we have collected about 150 grms. of rigorously pure samarium oxide. We also verified the different fractions, and found that they possessed absolutely the same characteristic spectra. Besides this, we thought it necessary to discover whether the atomic weight of the samarium remained constant at the end of another of these fractionations.

The determinations given in the accompanying table are the first which have been effected on samarium absolutely free from europium and gadolinium.

Our numbers, which differ very slightly from those of Clève, are higher than those which Demarçay obtained by the synthesis of the sulphate—a method in which he recognised decided irregularities.

In this latter method the majority of errors tend to diminish the atomic weight. On the other hand, the difference between the atomic weight of samarium and europium is so small that it would not explain the discrepancy between Clève's and Demarçay's numbers (150 and 148), because, in this case, Clève's samaria should not contain more than two-thirds of its weight of europium oxide, on account of the extreme rarity of this element. Further, if our numbers are slightly inferior to Clève's, this fact again points to the insufficiency of the method of synthesis by the sulphates employed by all Swedish chemists. Our method allows of very little error; the principle has

We conclude from these measurements that, admitting O=16, the atomic weight of samarium does not differ sensibly from the number 150'34. — *Comptes Rendus*, cxxxviii., No. 19.

A NEW METHOD FOR THE FRACTIONATION OF THE CERIC EARTHS.

By H. LACOMBE.

It being admitted that no method exists for quantitative separation in the rare-earth group, we can only have recourse to methods of fractionation to effect the separation of the simple elements forming this important series.

Of all the methods employed, fractional crystallisation of the salts in approved solvents gives the best results up to the present. This general method is the more successful as the salts used have the greatest differences in solubility from one element to the next. Now, these differences are greater, as a rule, in the case of the double salts than with the simple ones.

It was in this manner that Auer von Welsbach in 1885 (*Mon. f. Chem.*, vol. vi., p. 477), by fractionating the double ammoniacal nitrates of the earths of didymium,

succeeded in separating the lanthanum from the didymium and in splitting up this latter body into two component parts, praseodymium with green salts and neodymium with pink salts. However, a time comes, while carrying out this separation, when the fractions not sensibly containing lanthanum give syrupy solutions uncrystallisable even in concentrated nitric acid. In such a case Auer recommended the preliminary elimination of the yttric earths, which accumulate in the latter portions by fusion with nitrates, than to fractionate the raw, impure neodymium obtained in the form of the double sodic salt after having mixed it with a certain proportion of pure lanthanum, of which the action is to carry down the last traces of the praseodymium. Considering the relatively great difficulties met with in the preparation of pure lanthanum, the addition of this body to the neodymium appears to be rather audacious, and chemists who have prepared the rare earths in a state of purity are not, as a rule, very much disposed to re-mix the substances obtained at the cost of so much time and labour.

More recently, Demarcay (*Comptes Rendus*, vol. cxxx., p. 1019) has given an excellent method for the separation of samarium from neodymium by fractional crystallisation of the double magnesium nitrates in concentrated nitric acid. This method enables us easily to get rid of the properly called ceric earths from the yttria earths, from yttrium to samarium included. It can be substituted with great advantage for the fusion methods described by Auer. However, the double nitrates of magnesium do not easily lend themselves to the separation of the components of the old didymium.

Consequently, in the hope of obtaining an easier separation, I have endeavoured to find a salt whose solubility was less than that of the double alkaline nitrates, and greater than that of the double nitrates of magnesium. The double nitrate of manganese, corresponding to the type $2\text{Di}(\text{NO}_3)_3 + 3\text{Mn}(\text{NO}_3)_2 + 24\text{H}_2\text{O}$, is the one that has given me the best results. My experiments have been carried out successively on earths rich in neodymium and on earths rich in praseodymium.

In both cases the double nitrates of didymium and manganese are best fractionated in nitric acid of density 1.3.

The proportion of mother-liquors ought to be kept practically constant, and always in small quantity compared with the crystals. During the concentrations we sometimes observe a slight decomposition of the nitrate of manganese with the formation of the brown peroxide. In such a case it suffices to add a few drops of fuming nitric acid to the warm liquor, and it immediately becomes clear by the reduction of the peroxide of manganese, which is then dissolved instantly. To prevent supersaturation and to cause a slow crystallisation, it is as well to start the crystals with a nucleus of the double nitrate of bismuth and manganese, a salt isomorphous with those of the rare earths.

Earths Rich in Neodymium.—In twenty-four hours I obtained three consecutive fractions. The mother-liquors of Fraction 3 gave an intense absorption spectrum of samarium, and very slightly the band $\lambda = 525$, which is characteristic of neodymium. The samarium obtained in this manner was thus fairly pure. The proportion of neodymium, which can be detected by absorption under these conditions, being about a thousandth.

This separation of samarium is still more rapid and more decided than that proposed by Demarcay. It enables us to separate samarium from neodymium as easily as the use of the double nitrates enables us to separate nickel and cobalt, for example.

After having eliminated the samarium in this manner, I continued the fractionation so as to obtain eight consecutive fractions. The first six showed the praseodymium bands very distinctly. The crystals from the seventh fraction, dissolved in their water of crystallisation and examined through a thickness of 6 centimetres, hardly showed the characteristic blue bands of this element, while the very faint blue bands of neodymium were very distinct.

The eighth fraction was free from praseodymium, and its oxide was sky-blue in colour.

Earths Rich in Praseodymium.—This fractionation was continued until ten fractions were obtained. The first was decidedly green. The colour of the praseodymium masks that of the manganese. The following fractions had an undecided tint, and the last had the characteristic carmine colour of these salts of neodymium. Fraction 1 showed no trace of neodymium bands by absorption. The fractionation was continued by successively eliminating the fractions at one end containing no more neodymium, and the fractions at the other end containing no more praseodymium. After three hundred series of crystallisations, the proportion of intermediate fractions was reduced to such a point that the fractionation could no longer be carried out. This is the first time to my knowledge that in a separation of neodymium and praseodymium, the proportion of the intermediate fractions has been brought to a negligible point compared with the quantities of the elements separated at the two extremities of the fractionation.

The small quantity of lanthanum present in my earths was all accumulated in the first fractions.

I have further applied this method to earths containing much lanthanum and some fair amount of didymium; with five fractions only I completely eliminated the didymium from the first three fractions.

I am not prepared to pronounce very definitely as to the value of my method from the point of view of the separation of praseodymium and lanthanum. Still, I have observed that it can be effected.

To sum up, the method I propose enables us to eliminate samarium still more rapidly than by Demarcay's method, and it has incontestable advantages over that of Auer, so far as the separation of neodymium and praseodymium is concerned, since it enables us to reduce the portions intermediate between these two elements to very small quantities in proportion to the elements obtained in a state of purity.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 10.

INFLUENCE OF THE PHYSICAL NATURE OF THE ANODE ON THE CONSTITUTION OF ELECTROLYTIC PEROXIDE OF LEAD. APPLICATION TO ANALYSIS.

By A. HOLLARD.

We have already shown (*Bull. Soc. Chim.*, vol. xxix., p. 151) that the peroxide of lead deposited on a platinised platinum anode, in a saline solution of lead traversed by an electric current, is always accompanied by a notable amount of superoxides. In fact, the analytic factor by which the weight of peroxide deposited must be multiplied, to obtain the corresponding weight of lead, is lower than the ratio $\frac{\text{Pb}}{\text{PbO}_2} = 0.866$ of the molecular weights of lead

and of its binoxide. This analytic factor varies, according to a perfectly regular curve, with the concentration of the lead in the bath; the extreme values we have measured are 0.740 and 0.861, which correspond to 0.01 and 10 grms. of lead for a volume of 300 c.c. of the bath.

We have repeated these experiments with the same bath and the same strength of current, but substituting for the platinised platinum anode an anode of platinum roughened by a sand-blast. The analytic factor then takes a constant value equal to 0.833, no matter what the concentration of the bath may be. This figure being lower than 0.866 indicates the presence of superoxides accompanying the PbO_2 .

Thus with an anode of platinised platinum, the phenomena of superoxidation are very strongly marked with weak solutions of lead and only slightly pronounced with strong concentrations. On the other hand, with an anode of depolished platinum, the phenomena of superoxidation

remain constant no matter what the concentration may be. Again, the deposits behave differently; with platinised platinum the deposits are very compact no matter what quantity of lead there may be; with depolished platinum we can hardly deposit more than 1 grm. of lead in the form of peroxide.

However, this latter quantity of lead is generally sufficient in analysis, therefore we recommend the use of depolished platinum for the analysis of lead rather than use platinised platinum which necessitates the use of a curve to find the analytic factor.

We cannot use polished platinum, as the peroxide of lead will not stick to it.

The following tables give a summary of the experiments which gave us the factor 0.853 with depolished platinum. Our electrode of platinum gauze served as an anode in these experiments.

The experimental conditions of Table I. are identically the same as those described already (*Bull. Soc. Chim.*, vol. xxix., p. 151); the lead was in the form of nitrate dissolved in an excess of nitric acid.

The experiments in Table II. were made for the purpose of measuring the analytic factor when the lead is in the form of sulphate. For this purpose the sulphate of lead is dissolved in nitrate of ammonia and nitric acid, or, to be more exact, in the following mixture:—40 c.c. of ammonia (density = 0.924) and 67 c.c. of nitric acid (density = 1.33). As in Table I. the bath contained 10 grms. of copper in the state of nitrate.

I. Solution of Nitrate of Lead.

Lead weighed	Factor, $\frac{\text{Pb}}{\text{PbOx}}$
1.0004	0.8555
0.5001	0.8533
0.2005	0.8543
0.1006	0.8532
0.0698	0.8477
0.0500	0.8532
0.0301	0.8551
0.0103	0.8483

The mean of these results is 0.853.

II. Solution of Sulphate of Lead.

	Factor
0.1002	0.8579
0.2999	0.8549
0.5001	0.8507
0.9996	0.8485

Mean = 0.853.

—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 5.

THE FORMATION OF BASIC SALTS OF COPPER UNDER THE INFLUENCE OF ELECTROLYSIS.

By ANDRÉ BROCHET.

WHEN we electrolyse a solution of chlorate of copper, using an anode of this metal, we notice the formation of basic salts containing a certain amount of chloride, as does also the solution. The metallic deposit obtained at the negative pole is a bad one, without cohesion and also containing chloride.

The anode is eaten away in the same manner as in the electrolysis of chlorate of potassium; it is pitted at numerous points, and eventually becomes perforated, while other parts remain entirely unattacked. By continuing the operation for a sufficiently long time the anode is transformed into a sort of lace work.

These experiments were carried out in the apparatus already described in the paper on the action of copper on chloric acid, some at the ordinary temperature, and others at the temperature of the water-bath.

The conditions were the same as in the case of the

electrolysis of chloric acid; the intensity of the current was 4 ampères for a metallic strip of 1 square decimetre. The back pressure was zero, naturally, and the electromotive force about 2 volts. The solution of chlorate of copper used contained half a grm.-molecule per litre.

The pale blue precipitate formed, and of which a certain quantity adheres to the anode, is whiter in the lower parts. If we filter the solution on the one hand, and on the other hand rapidly wash the anode with a dilute solution of nitric acid (60 c.c. per litre), having no sensible action on the copper and consequently no reducing power on the chlorate, we observe on estimation:—

1. That the amount of copper at the anode is greater than that deposited in the voltameter.
2. That the precipitate and the solution contain a certain quantity of chlorine in the form of chloride.
3. That the amount of chloride formed is greater than that corresponding to the reduction of the chlorate of copper, admitting that the cathodic reduction takes place in this manner, which, however, is not the case since there is a deposit of copper difficult to estimate.

The ratio of the weight of copper to the weight of chlorine in the form of chloride is greater than in the form of chloric acid; this is because of the precipitation of the copper, and consequently little or no reduction of the chlorate.

The electrolysis of chlorate of copper, complicated in appearance, becomes very simple when we know the action of copper on chloric acid and chlorate of copper.

In a previous paper I examined the first of these reactions, and have already referred to the second, which, however, requires some complementary explanation.

The reduction of chlorate of copper by copper, either in a strip or as turnings, always takes place in the same manner. All that varies is the speed of the reaction. In every case the copper becomes covered with a layer of cuprous hydrate. Apparently this product is formed simultaneously with cupric chloride. The cuprous hydrate becomes oxidised at the expense of the chlorate.

The cupric oxide thus formed unites with the chloride to form a basic salt, but as it is in great excess it also precipitates a certain quantity of chlorate, forming a mixed basic compound. We observe, in fact, that at the commencement of the reaction there is a certain quantity of chloride in solution, and that after some time this salt has almost entirely disappeared.

The compound obtained by electrolysis is formed as before of chlorate and chloride, as is easy to show.

The powders obtained by the two processes, dissolved in nitric acid, give an abundant precipitate with nitrate of silver; both give oxidised compounds of chlorine with sulphuric acid, but while the salts obtained by electrolysis deprecipitate with violence, the others have only a very slightly energetic action.

All these salts have not the same composition, but in each the ratio Cu:Cl is practically constant and corresponds to the formula given for the basic chloride of copper.

The different products obtained by the action of copper on the chlorate, with or without electrolysis, thus answers to the formula— $\text{Cu(A)}_2\cdot 3\text{Cu(OH)}_2$, in which Cl and ClO_3 can be substituted one for the other in A_2 . But when the salt obtained by the direct action of copper on the chlorate contains principally chloride, which explains the absence of this latter salt in solution, as we have seen, the electrolytic product contains almost as much chlorate as chloride; on the other hand, the solution is then richer in chloride. These differences have to do, perhaps, with the greater or less richness of the solution in chlorate; they explain the difference in the action of concentrated sulphuric acid.

Conclusions.—The action of copper on chlorate of copper is identical with that which it exercises on chloric acid. Both one and the other are produced successively

when we react with the metal on chloric acid with or without the help of electrolysis.

As soon as the acid is saturated the chlorate comes into play, but the speed of the reaction is much less. There is formed on the one hand the cupric salt, on the other the cuprous salt, now the chloride, now the hydrate; in certain cases, perhaps even always, a mixture of the two.

These salts of copper became oxidised at the expense of the chlorate; according to the acidity of the solution the hydrate dissolves or remains precipitated, carrying with it the chlorate or the chloride in the form of mixed basic salts. It follows that the ratio of the dissolved copper to the copper precipitated in the voltameter varies from 1.5 to 2 according to the conditions.—*Bull. Soc. Chim.*, Series 1, vol. xxxi., No. 6.

THE SEPARATION OF IRON FROM NICKEL AND COBALT BY LEAD OXIDE (FIELD'S METHOD).*

By T. H. LABY,

Junior Demonstrator of Chemistry, University of Sydney.

REVIEW OF METHODS FOR THE SEPARATION OF IRON FROM NICKEL AND COBALT.

1. Ammonium Hydrate and Chloride.

THE precipitation of ferric salts by ammonium hydrate in the presence of ammonium chloride gives an incomplete separation—according to Moore an absolutely worthless one (*CHEMICAL NEWS*, 1892, lxxv., p. 75). No experimental work on the re-precipitations necessary for accuracy was found. Fresenius states three to be necessary. Baumhauer is said to have found that ferric hydrate may occlude 27 per cent of nickel and 48 per cent of cobalt (*Archives fur Néerlandaises*, 1870, vol. vi., reference not verified).

2. Ammonium Carbonate (Schwarzenberg, *Liebig's Annalen*, xlvii., p. 216; also *Chem. Gaz.*, 1856).

To the solution of the chlorides, containing ammonium chloride equal to twenty times the weight of the oxide of nickel present, ammonium carbonate is added to a point specified in Schwarzenberg's paper, and quoted by Fresenius. The success of the method depends on striking a point difficult to ascertain. The method, however, is recommended by Fresenius and others. The writer, in an analysis of a meteoric iron, found it to be a long and tedious separation; and the amount of nickel found being lower than by Field's method, partly owing to a slight loss in the precipitation of the nickel as sulphide and subsequent electrolysis. In this and the previous method the presence of much ammonium chloride makes the solution unsuitable for the immediate determination of the nickel by electrolysis. The solubility of the sulphide in excess of ammonium sulphide may make the sulphide precipitation inaccurate (Terril, *Chem. Gaz.*, 1857).

3. Basic Acetate.

Kessler uses a solution containing 1 gm. of ferric iron per 500 c.c., and adds 1 gm. each of acetic acid and sodium acetate (*Ber.*, also *CHEMICAL NEWS*, xxvii., 14). The presence of much of the latter caused the iron to carry down manganese. Meineke adds a small quantity of acetic acid and sodium acetate to a neutral solution, and gives a short rapid boil (*Zeit. Angew. Chem.*, 1888, [2], xix., 232). Mackintosh believes ammonio-cobalt bases are formed which are peroxidised, finding five or six precipitations necessary; and that cobalt is more difficult to separate than nickel (*School of Mines Quarterly*, July, 1887). Moore says four precipitations are necessary (*CHEMICAL NEWS*, 1892, lxxv., 75). Brearley, who has done much to elucidate

the acetate process, found, for a ratio first determined by Kessler, that the solution produced by carefully adding sodium or ammonium carbonate to a cool ferric chloride solution till incipient precipitation, contains then about seven-eighths of the ferric chloride as "dissolved hydrate." Brearley (*CHEMICAL NEWS*, 1899, lxxix., 194; 1897, lxxvii., 210) adds sodium or ammonium carbonate to the cool ferric and nickel chlorides, &c., till a slight permanent precipitate forms, 10 c.c. of 5 E. (or 5 normal) acetic acid, water to about a litre, then 10—12 c.c. of 0.36 E. ammonium or sodium acetate for each gm. of iron present, and raises to the boiling-point. He showed the separation is for total dissolved hydrate solutions most nearly complete when this small amount of acetate is used. Either the sodium or ammonium salts may be used. An increase of acetic acid tends to improve the separation, while an increase of acetate retards it; for example, taking 1.0 gm. of iron, 0.1 gm. of nickel, 10 c.c. of 5 E. acetic, and 10 c.c. of 4.4 E. ammonium acetate (122 c.c. of 0.36 E.) only 0.0884 gm. of nickel was recovered. His results show the acetate may be better added to a boiling solution than a cold one, though this is opposed to the usual custom. Contrary to the opinions of Moore and Mackintosh, his results would show cobalt to be more readily separated from iron than nickel is. The acetate and acetic acid mentioned first above, was insufficient for 1.0 gm. of iron in the presence of 0.1 gm. of aluminium, but 60 c.c. were necessary, and only 98 per cent of the nickel was then recovered. Nickel acetate though soluble in ammonium chloride is insoluble in acetic acid. Ferric acetate is decomposed at 100° C. into the hydrate and acetic acid.

4. Phosphate Method.

Cheney and Richards (*Am. Journ. Sci.*, [3], xiv., 178—181, and *CHEMICAL NEWS*, 1877) precipitated the ferric iron by sodium phosphate in the presence of acetic acid. With more than 3 per cent of nickel re-precipitation was necessary, 99 per cent of the nickel was recovered. Moore, nine years later, apparently independently, published the same method recommending two precipitations for accurate work, but gave no test analysis (*CHEMICAL NEWS*, 1886, liv., 309).

5. Electrolysis.

Le Roy (*Comptes Rendus*, cxii., 772—3) deposits the nickel, cobalt, and iron from an ammonium citrate, sulphate, and hydrate solution, replaces it by a sulphate and hydrate one, and then reversing the current re-dissolves and re-precipitates the nickel and cobalt, while the iron goes into suspension as ferric hydrate. No confirmatory results are given. Engels states that nickel may be deposited free from iron if the latter is thoroughly oxidised by hydrogen peroxide (*Journ. Chem. Soc.*, Abs., 1898, ii., 192; "Rundschau," 1896, 20—24). Foerster finds iron to be deposited (*Journ. Chem. Soc.*, 1898, ii., 228). Ducru obtains the nickel, cobalt, and iron (ferric) as sulphates, and electrolyses in the presence of the ferric hydrate precipitated by the free ammonia present (*Bull. Soc. Chim.*, 1897, [3], xvii.). An irregular amount of iron, about 0.5 per cent of the total present, is deposited with the nickel, partially insoluble in concentrated hydrochloric acid. Using the usual sulphate solution Neumann finds (*Chem. Zeit.*, 1898, [72], xxxii., 731—732), contrary to Engels and Ducru, that with varying conditions of time and strength of current a quite irregular amount of iron is deposited (if more than 0.1 gm. of iron as ferric hydrate is present), which is tedious and inaccurate to determine volumetrically.

6. The Ether Process.

The solubility of ferric chloride, and insolubility of manganese, nickelous, chromic, and aluminium chlorides in ether in the presence of hydrochloric acid, was pointed out by Rothe in 1892 (Abstract in *CHEMICAL NEWS*, 1892, lxxi., 182; "Mitth. a. d. Kgl. Tech. Versuchs," Anstalten, Berlin), who used it as a means of separating iron from cobalt, copper, and these metals. Copper and cobalt partly

* Read before the Royal Society of N. S. Wales, September 3, 1903. From the *Journal and Proc. Royal Society of N. S. W.*, xxxvii., p. 157.

in solution in the ether may be removed by shaking out the ether with 5 g. E. (S.G. 1.104) hydrochloric acid. A modification of this is the solution of the chlorides (0.4 grm.) in a minimum of water, and 10 c.c. of concentrated hydrochloric acid, the addition of 10 c.c. of ether, and the passing into it of hydrochloric acid gas at 0° C. (Pinerua, *CHEMICAL NEWS*, 1897, lxxxv., 103). The nickel is precipitated as the yellow chloride; the iron and cobalt are in solution. Adaptations for technical work, nickel steel and ores, have been published. Langmuir (*Journal Am. Chem. Soc.*, vol. 1, 1900) precipitates the iron with ammonium hydrate (the sulphuric acid present in the case of some ores, &c., interferes with the ether extraction) before applying the separation of the chlorides. Acetone may be added to the ether (Norris, *Journ. Soc. Chem. Ind.*, 1901, xx., 6). The separation has been elucidated by Speller (*CHEMICAL NEWS*, lxxxiii., 124; Sargent, *Journ. Am. Chem. Soc.*, October, 1899, 854). A minimum of hydrochloric acid of strictly 1.1—1.11 S.G. should be used to dissolve the chlorides, 5 c.c. of ether being added per 0.1 grm. of Fe. Two separations are made. The ether extraction process has yet to be tested as thoroughly as Kern tested it for iron from uranium (*Journ. Am. Chem. Soc.*, 1902, xxiii., 10). A slight alteration of the concentration of the reagents affects considerably the behaviour of the cobalt.

7. Field's Process.

Field proposed the method examined in the following experiments (*CHEMICAL NEWS*, 1859, i., 4). It is based on the precipitation by litharge of iron as ferric hydrate from a neutral solution of the nitrates of iron, nickel, and cobalt. He gave two results of test analyses in support for nickel, but none for cobalt. Cheney and Richards (*CHEMICAL NEWS*, 1877, xxxvi., 161) found "by far the best success was obtained in the use of the method given by Field," but Moore says "Field's process . . . cannot be recommended" (*CHEMICAL NEWS*, 1886, liv., 306).

Experimental—Advantages of Field's Method.

An inquiry into the accuracy of Field's method was made, as it had distinct advantages over methods commonly in use, viz., a single precipitation of the iron, and the absence, after the removal of the added lead, of all reagents such as ammonium or sodium salts. When combined with the electrolytic determination of nickel and cobalt the method becomes more rapid than, say, a double precipitation of the iron by the basic acetate process and the precipitation of the nickel and cobalt as sulphides. The electrolytic determination, which is highly accurate and convenient, cannot be readily combined with the acetate process, as some experimenters find that ammonium chloride is detrimental to the deposition of the nickel and cobalt ("Electrolytic Methods of Analysis," Neumann; but compare Oettel, *Zeitschr. f. Electrochem.*, 1894, i., 194).

Test Analyses.

In the following experiments, Table I., the amount of iron mentioned was taken in the form of a solution of the nitrate together with cobalt or nickel nitrates, and evaporated in a porcelain dish on a water-bath to dryness. It was found that the iron is precipitated as ferric hydrate most readily when the evaporation is stopped just before dryness, and the formation of a very basic nitrate of iron is avoided. The residue from the evaporation was diluted, brought to the boil, and the lead monoxide added while the solution was boiling either in the dish or preferably in a conical flask. On the addition of sufficient lead oxide (six times the weight of the iron present) ferric hydrate separated out in a form which was readily filtered; but often the washing was most tedious, and some of the precipitate passed through the filter-paper. In the first experiments hot water was used, but it was found better, as would be expected, to wash with a solution of some salt, lead nitrate being the one used. The presence of a small quantity of ferric hydrate does not interfere with the accuracy of the

electrolytic deposition of nickel and cobalt. The filtrate contains the nitrates of lead and cobalt or nickel. This lead was removed in some cases by evaporating the filtrate nearly to dryness, adding an excess of sulphuric acid, 50 c.c. of 5 E. to every 1—2 grms. of lead present, decomposing the nitrates, diluting, and finally filtering off the lead sulphate. In the case of experiments 5, 6, 8, and 9, Table I., 6, 7, 8, and 9, Table II., the lead sulphate precipitated from the boiling solution by 50 c.c. of 5 E. H_2SO_4 was filtered off without expelling the nitric acid. After adding an excess of ammonium hydrate these filtrates were electrolysed.

Standard Solutions of the nitrates of iron, nickel, and cobalt were prepared:—

Nitrate of iron from iron wire containing 0.07 per cent of carbon.

Nitrate of Cobalt: 25 grms. of cobalt sulphate and 50 grms. of ammonium sulphate were dissolved in water, made very slightly acid, sulphuretted hydrogen passed through the solution, and the resulting precipitate removed. The filtrate was made alkaline with ammonium hydrate, and boiled for a long time in order to remove the iron as ferric hydrate. On electrolysis this solution gave a dull grey firmly adherent deposit, which was weighed, dissolved in nitric acid, and the solution made to a known volume. This purification would give a cobalt nitrate sufficiently free from all impurities, excepting nickel.

TABLE I.—Cobalt.

No	Iron taken. Grm.	Cobalt taken.	Cobalt found.	Error	
1.	0.004	0.2289	0.2293	+0.0004	
2.	0.004	0.2289	0.2290	+0.0001	
3.	none	0.2289	0.2287	-0.0002	
4.	0.2	0.2289	0.2253	-0.0036	Cobalt not completely removed by electrolysis.
5.	0.2	0.2389	0.2266	-0.0123	
6.	0.2	0.2289	0.2178	-0.0111	Cobalt not completely removed by electrolysis. (a)
7.	0.2	0.2289	0.2221	-0.0068	
8.	0.2	0.2229	0.2235	+0.0006	
9.	0.2	0.2229	0.2238	+0.0009	
10.	none	0.0458	0.0466	+0.0008	
11.	none	0.0229	0.0235	+0.0006	

(a) This filtrate, though electrolysed all night and for three hours with 0.8 ampères, still contained cobalt, as was shown by passing sulphuretted hydrogen.

TABLE II.—Nickel.

No	Iron taken. Grm.	Nickel taken.	Nickel found	Error	
1.	0.004	0.2149	0.2145	-0.0004	
2.	0.004	0.2149	0.2123	-0.0026	Ferric hydrate contained nickel.
3.	none	0.2149	0.2147	-0.0002	
4.	0.2	0.2149	0.2114	-0.0035	Iron precipitated by PbO from boiling solution.
5.	0.2	0.2149	0.2100	-0.0049	Iron precipitated by PbO in the cold.
6.	0.2	0.2149	0.2122	-0.0027	Iron precipitated by PbO from boiling solution.
7.	none	0.2149	0.2155	+0.0006	Pb added and removed as sulphate.
8.	0.4	0.0430	0.0454	+0.0024	
9.	0.4	0.0430	0.0451	+0.0021	
10.	none	0.0430	0.0439	+0.0009	
11.	none	0.0219	0.0224	+0.0005	

Nitrate of nickel* was prepared similarly. The flasks and pipettes used were calibrated against calibrated weights. Judging from the greatest difference between the values obtained for any one pipette in this testing, the amounts of cobalt and nickel "taken" are never inaccurate by more than ± 0.0001 gram.

The equation for the reaction was found to be essentially $3\text{PbO} + 2\text{Fe}(\text{NO}_3)_3\text{Aq} = 3\text{Pb}(\text{NO}_3)_2 + \text{Fe}_2\text{O}_3\text{Aq}$. Thus the lead oxide used should be at least six times the weight of iron to be precipitated. In each of the test analyses, slightly more than six times as much lead oxide was used. An excess of 20 c.c. of 17 E. ammonium hydrate was used in each electrolysis.

Conclusions.

This method, requiring only one precipitation of the iron, though not so good as claimed by Field, is more accurate for cobalt than the basic acetate process; and as accurate for nickel—about 99 per cent of the latter, and rather more of the former being recovered. It can be very readily combined with the electrolytic determination of nickel and cobalt. Gooch and Medway (*Am. Journ. Sci.*, 1903, xxv, 50) using a rotating cathode, have accurately determined nickel by electrolysis with a current of less than thirty minutes' duration.

The author desires to thank Prof. Liversidge for having given every facility for this research.

REPORT ON THE DETERMINATION OF NITROGEN.[†]

By F. W. MORSE.

THE author, in accordance with the vote of the Association last year, undertook the comparison of methods for determining the availability of organic nitrogen. Two methods were recommended by the previous referee for trial, namely, the neutral permanganate method, as modified by Mr. Street, and the alkaline permanganate method as modified by Mr. Jones. The former has been adopted by this Association as a provisional method, while the latter has not been regarded with much favour by the majority of analysts who have tried it.

Since nearly all the principal nitrogenous fertiliser materials have been worked upon in the past by the different methods, the author considered it the best policy this year to confine the work to two typical materials combined with superphosphate in approximately the proportion which might occur in a mixed fertiliser, in order to determine how closely results by different analysts would agree, and to make plainer any defect in the manipulation of the method.

The materials selected were dried blood and cotton-seed meal, because both are known to be highly available to plants, while the alkaline method has always failed to indicate the availability of cotton-seed meal, owing apparently to its carbonaceous matter. The blood was a part of a bag of blood meal for poultry and calves, and contained 13.1 per cent of nitrogen. The cotton-seed meal was a standard brand, and contained 7.49 per cent of nitrogen.

Four lots of material were prepared, containing approximately 3.5 to 4 per cent of nitrogen. The mixtures all contained superphosphate, while the nitrogenous material was arranged as follows:—No. 1, blood; No. 2, cotton-seed meal; No. 3, two-thirds nitrogen from blood, one-third nitrogen from cotton-seed meal; No. 4, one-third nitrogen from blood, two-thirds nitrogen from cotton-seed meal.

All the materials were sifted through the standard sieve, with circular holes 1 m.m. in diameter, and then each lot

TABLE I.—Total Nitrogen.

Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Remarks.
Per cent.	Per cent.	Per cent.	Per cent.	
T. C. Trescott, Washington, D.C. :—				
3.78	3.30	3.82	3.73	Digested two hours.
3.75	3.34	3.85	3.73	
3.98	3.59	3.95	3.87	Digested three hours.
4.09	3.60	3.95	3.85	
Department of Foods and Feeding, Hatch Experiment Station, Massachusetts :—				
4.16	3.58	4.01	3.84	Digested three hours, Kjeldahl method.
4.16	—	3.99	3.84	
4.15	3.56	3.97	3.81	
4.17	3.64	4.07	3.96	Digested three hours (Kjeldahl) with sulphate of potash.
4.14	—	4.06	3.92	
4.14	3.63	4.03	3.92	
F. B. Carpenter, Virginia :—				
4.18	3.59	4.06	3.97	
S. H. Sheib, Virginia :—				
4.19	3.55	4.07	3.94	
L. A. Hill, New Hampshire :—				
3.90	3.54	—	3.67	Digested three to four hours.
3.98	—	—	3.78	
4.00	3.54	3.89	3.73	
W. W. Braman, New Hampshire :—				
3.98	3.45	3.88	3.84	
4.03	3.48	3.94	3.86	
A. L. Sullivan, New Hampshire :—				
4.05	3.33	3.92	3.64	Gas pressure lower than normal.
4.06	3.33	3.89	3.72	
J. Bernard Robb, Maryland :—				
4.03	3.50	3.95	3.77	Digested one hour.
4.05	3.47	3.93	3.79	
4.08	3.51	3.96	3.82	
C. H. Jones, Vermont :—				
4.32	3.69	4.04	4.04	Digested two and a-half to three hours.
4.35	3.69	4.04	3.97	
4.32	3.76	4.11	3.97	
F. W. Woll and Geo. A. Olson, Wisconsin :—				
4.16	3.58	4.01	3.93	Digested from one and a-half to five hours.
4.19	3.58	4.01	3.98	
4.17	3.60	4.08	3.95	
4.14	3.57	4.07	3.95	
—	—	4.09	—	
W. H. Scherrfins and A. M. Peter, Kentucky :—				
4.08	3.49	3.97	3.79	Digested three hours.
4.07	3.53	3.88	3.86	
4.13	3.54	3.95	3.86	Digested five hours.
4.12	3.54	3.94	3.87	
W. R. Perkins, Mississippi :—				
4.02	3.48	3.89	3.90	

was thoroughly mixed. The blood was apparently coarse, because a large part of it was crystalline rather than fibrous. Two of the analysts re-ground the samples containing it.

Twelve lots of samples were sent to as many different laboratories. Accompanying the samples were sent the following instructions:—

Directions for Work on Nitrogen, 1902.

Please determine total nitrogen in each sample by either of the official methods. Last year the referee called attention to the fact that prolonged digestion with the sulphuric acid in the Kjeldahl method raised the amount of nitrogen. Please note the length of time used in each digestion throughout the comparison. Please determine available nitrogen by the neutral permanganate method adopted provisionally at the last convention, and by Jones's alkaline permanganate method, which has so far been regarded

* Foerster, *Zeit Electrochem.*, 1897, iv., 160–165. C, Si, Cu, Mn entirely absent from electrolytically deposited Ni, Fe, and Co in same proportion as unrefined material.

† Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

TABLE II.—*Insoluble Nitrogen (Neutral Permanganate Method).*

Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Remark.
Per cent.	Per cent.	Per cent.	Per cent.	
T. C. Trescott, Washington, D.C. :—				
0.68	0.37	0.94	0.72	Washed.
0.80	0.25	0.86	0.83	
1.90	0.46	0.91	0.60	Not washed.
1.78	0.25	0.72	0.81	
Department of Foods and Feeding, Hatch Experiment Station, Massachusetts :—				
1.85	0.40	1.22	0.93	
1.78	0.39	1.15	0.83	
S. H. Sheib, Virginia :—				
0.65	0.30	0.56	0.61	
L. A. Hill, New Hampshire :—				
0.42	0.31	0.70	0.84	Not washed.
0.46	0.56	0.78	0.80	
0.53	0.23	0.49	0.52	
0.61	0.31	0.50	0.40	
W. W. Braman, New Hampshire :—				
0.92	0.56	0.87	0.77	
0.40	0.36	0.56	0.52	
A. L. Sullivan, New Hampshire :—				
1.01	0.38	0.67	0.50	
1.28	0.41	0.67	0.52	
C. H. Jones, Vermont :—				
1.29	0.35	1.06	0.87	
F. W. Woll and Geo. A. Olson, Wisconsin :—				
0.34	1.17	1.04	1.52	
0.36	1.12	0.99	1.55	
W. H. Scherffins and A. M. Peter, Kentucky :—				
0.39	1.20	0.97	1.51	
1.26	0.45	1.48	0.97	
1.47	0.49	1.33	0.76	
1.26	0.36	1.53	0.83	
1.34	0.32	1.05	0.91	
W. R. Perkins, Mississippi :—				
0.59	0.41	0.70	0.71	
0.59	0.41	0.68	0.64	

unfavourably. The latter method used in accordance with Mr. Jones's practice offers some advantages over the former in the matter of time. The methods are described as follows :—

The Neutral Permanganate Method.—Into a 400 c.c. Griffin beaker, low form, weigh an amount of sample containing approximately 0.075 grm. of nitrogen (samples containing material that has been treated with acid should be washed on a 9 c.m. S. S. No. 595 filter to 200 c.c. and transferred, filter and all, to beaker). Digest this with 125 c.c. of permanganate of potash solution (16 grms. of pure KMnO_4 to 1000 c.c. of water) in a steam- or hot-water bath for thirty minutes. Have the beaker let down well into the steam or hot water, and keep closed with a cover glass, stirring twice at intervals of ten minutes with a glass rod. At the expiration of the time, remove from bath, add 100 c.c. of cold water, and filter through a heavy 15 c.m. folded filter. Wash with cold water, small quantities at a time, till total filtrate amounts to 400 c.c. Dry, and determine nitrogen in residue by Kjeldahl method.

The Alkaline Permanganate Method.—Weigh out an amount of sample containing approximately 0.045 grm. of nitrogen, and transfer to a 600 c.c. distillation flask. After connecting with condenser to which the receiver containing standard acid has been attached, digest with 100 c.c. of alkaline permanganate solution (16 grms. of potassium permanganate and 150 grms. of sodium hydrate dissolved in 1000 c.c. of water) for thirty minutes below the boiling-point. Then boil slowly until the distillation is completed.

TABLE III.—*Soluble Nitrogen (Alkaline Permanganate Method).*

Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Remark.
Per cent.	Per cent.	Per cent.	Per cent.	
T. C. Trescott, Washington, D.C. :—				
2.46	1.57	1.99	1.68	
2.32	1.51	2.10	1.82	
Department of Foods and Feeding. Hatch Experiment Station, Massachusetts :—				
2.38	1.30	1.83	1.55	
—	—	—	1.53	
2.35	1.30	1.82	1.51	
L. A. Hill, New Hampshire :—				
2.73	1.82	2.31	1.82	Distilled very low.
2.80	1.96	2.38	2.13	
W. W. Braman, New Hampshire :—				
2.99	2.00	2.71	2.57	Distilled very low.
2.98	1.93	2.80	2.49	
A. L. Sullivan, New Hampshire :—				
2.90	2.44	2.41	2.26	Distilled very low.
2.97	2.27	2.57	2.54	
J. Bernard Robb, Maryland :—				
2.83	1.85	2.40	2.27	
2.88	1.84	2.46	2.17	
2.75	1.78	2.31	2.19	
C. H. Jones, Vermont :—				
2.67	1.50	2.16	1.86	
2.64	1.53	2.09	1.90	
F. W. Woll and Geo. A. Olson, Wisconsin :—				
2.22	1.28	1.81	1.77	
2.33	1.18	1.84	1.78	
2.27	1.40	1.96	1.75	
2.17	1.33	1.79	1.70	
W. H. Scherffins and A. M. Peter, Kentucky :—				
1.64	1.25	1.47	1.37	
1.79	1.25	1.41	1.36	
1.83	1.26	1.34	1.48	
W. R. Perkins, Mississippi :—				
2.81	1.56	2.31	2.05	
2.79	1.62	2.47	2.18	
2.75	1.54	2.34	2.07	

TABLE IV.—*Availability of Nitrogen in Neutral Permanganate.*

Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Remark.
Per cent.	Per cent.	Per cent.	Per cent.	
T. C. Trescott, Washington, D.C. :—				
81.63	91.36	77.21	80.05	Washed until neutral.
54.34	90.25	79.49	81.86	Unwashed.
Department of Foods and Feeding, Hatch Experiment Station, Massachusetts :—				
55.45	89.00	69.64	76.05	
57.21	89.15	71.24	78.53	
S. H. Sheib, Virginia :—				
84.49	93.52	86.24	81.97	
L. A. Hill, New Hampshire :—				
88.97	87.57	80.62	77.68	Unwashed samples.
85.75	92.38	86.85	87.94	Washed samples.
W. W. Braman, New Hampshire :—				
83.50	87.57	81.84	83.36	
A. L. Sullivan, New Hampshire :—				
71.85	88.28	82.82	81.70	
C. H. Jones, Maryland :—				
70.20	90.57	73.89	79.45	
F. W. Woll and Geo. A. Olson, Wisconsin :—				
91.36	67.31	75.30	61.26	
W. R. Perkins, Mississippi :—				
85.32	88.31	82.26	82.69	

TABLE V.—Availability of Nitrogen in Alkaline Permanganate.

	Sample No. 1. Per cent.	Sample No. 2. Per cent.	Sample No. 3. Per cent.	Sample No. 4. Per cent.
T. C. Trescot, Washington	59.30	42.89	51.64	45.53
Department of Foods and Feeding, Hatch Experiment Station, Massachusetts	57.26	56.22	45.45	40.00
L. A. Hill, New Hampshire	56.68	36.04	45.30	39.47
W. W. Brame, New Hampshire	69.17	53.39	61.53	52.95
A. L. Sullivan, New Hampshire	74.50	56.64	70.33	65.71
J. Bernard Robb, Maryland	72.34	70.57	63.84	65.21
C. H. Jones, Vermont	66.63	52.00	60.91	58.15
F. W. Woll and Geo. A. Olson, Wisconsin	61.31	40.88	52.34	47.12
W. R. Perkins, Mississippi	54.19	36.31	45.43	44.30
	69.23	45.21	61.01	53.84

Since the samples all contain superphosphates, it will be necessary to wash them as directed for the neutral method. This is not necessary for the alkaline method, as it is intended to be used. Comparisons of washed and unwashed charges will be appreciated, however.

The troublesome features of these methods seem to be filtration in the neutral and distillation in the alkaline method. Suggestions for hastening these steps will be of interest.

Results of Analyses.

The methods were copied from the report of last year.

Returns were received from nine laboratories, and included the work of twelve analysts. The accompanying tables give their results in full.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, May 27th, 1904.

Mr. J. SWINBURNE, Vice-President, in the Chair.

A PAPER entitled "*The Law of Action between Magnets and its bearing on the Determination of the Horizontal Component of the Earth's Magnetic Field with Unifilar Magnetometers*" was read by Dr. C. CHREE.

Starting with the general formula for the action between two magnets perpendicular to one another, in Lamont's first position, the paper discusses how observations should be combined when the higher terms usually neglected in magnetometer reductions are taken into account. It considers the effect of errors in setting the deflecting magnet or in the values assigned to the graduations of the deflection-bar, and of errors in the deflection-angles, according as observations are made at one, at two, or at three distances. Assuming a simple magnet to be replaceable by poles, and making use of formulæ due originally to Lamont and Birge, calculations are made as to the size of the several coefficients, P , Q , R , in the deflection formula, for hypothetical values of the pole-distance, in the magnets of the more usual English magnetometer types. These calculated values are compared with the mean values observed at Kew in past years in magnetometers of the several types; and conclusions are drawn as to the mean ratio of the pole-distance to the total length of the magnets. The question of variation in the pole-distance with time is dis-

cussed in connection with recorded mean annual values of the P coefficient for the observatory magnetometers at Kew, Batavia, and Mauritius. The paper concludes with the results of some experiments on the degree of uniformity in the pole-distance of magnets of the same size and pattern. The method consisted essentially in employing two magnets alternately as deflector and deflected in the same magnetometer. Instrumental peculiarities are in this way largely eliminated.

Dr. W. WATSON said that the author had referred in the course of his remarks to a statement which he (Dr. Watson) had made at a former meeting of the Society, to the effect that the limit of accuracy in the setting of the magnet-carriage upon the deflection-bar was 0.1 m.m. Although it might be possible, when working under favourable conditions at an observatory, to make the setting with greater precision, he thought that 0.1 m.m. was as much as could be expected or obtained in ordinary work in the field. He pointed out that the number of settings in a deflection experiment was a safeguard against inaccuracies in individual settings, and that it was probable that there was no source of constant error. He expressed his interest in the author's experiments on pole-distances, and said that when the magnetometers were being designed for the Indian Survey he had expressed the opinion that it might be advantageous to make the coefficient Q equal to zero by choosing suitable pole-distances for the magnets. Probably Dr. Chree's experiments will enable us to settle whether it is sufficiently accurate to make Q as small as possible and work with a value of P only, determined in the ordinary way.

Dr. P. E. SHAW pointed out that brass, which is used for the deflection-bar, has a specially large thermal expansion, and if 50 c.m. of it rises 3° C. the increase in length would be about 25 microns, which Dr. Chree stated to be the error in setting the magnet-carriage on the scale. Possibly some alloy, e.g., some form of invar, would be preferable to brass.

Prof. H. L. CALLENDAR said that some time ago he made some experiments upon the distance between the poles of magnets, and the conclusion he came to was that it was impossible to express the pole-distance as a definite fraction of the length of the magnet. He had found that among other things the pole-distance depended upon the shape of the magnet, the intensity of magnetisation, and the kind of steel of which the magnet was composed. There was also a variation of the pole-distance with time.

Mr. SKINNER said that it might be possible to fix the position of the poles by using magnets similar to those used by Mr. Searle in many of his experiments. These magnets consisted of long thin needles with steel balls at the ends, and it was found that the poles were very close indeed to the centres of the balls.

Dr. CHREE said that the limit of accuracy in the setting of the magnet carriage which he had mentioned, 0.03 m.m., was that which was obtainable when working under the most favourable conditions. With regard to the material of the deflection-bar, he pointed out that a sufficiently accurate temperature correction was always employed to correct for thermal expansion. There was no invar which was sufficiently non-magnetic to be used in accurate work with a magnetometer.

A paper "*On the Ascertained Absence of Effects of Motion through the Æther in relation to the Constitution of Matter on the FitzGerald-Lorentz Hypothesis*," by Prof. J. LARMOR, was taken as read.

In consequence of recent misapprehensions (cf. D. B. Brace, *Phil. Mag.*, March, 1904), the argument on this subject, as given in "*Æther and Matter*" (1900), is briefly re-stated. The absence of effect of convection, to the first order, was demonstrated by Lorentz. Absence of effect to the second order of the ratio of the velocity of convection to that of radiation has now been experimentally established, as regards optical interference with long path, by Michelson; as regards mechanical action on a charged electric con-

denser, by Trouton; as regards double-refraction, by Lord Rayleigh and by Prof. Brace. This suggests strongly a complete correspondence in detail between the material system connected with the earth's motion and the same system at rest in the ether, so that their internal relations are indistinguishable. Theoretically such complete correspondence, up to the second order, exists, involving the Fitzgerald-Lorentz shrinkage, provided a purely electrical constitution of matter (as regards its physical relations) is granted, but apparently not otherwise. Thus it is held that these phenomena point consistently in that direction.

A paper "On Coherence and Recoherence," by Dr. P. E. SHAW and Mr. C. A. B. GARRETT, was read by Dr. SHAW.

In a paper in the *Phil. Mag.* (March, 1901), Dr. Shaw described a method of investigating coherence by measuring the forces required to sunder the cohored surfaces. It was there shown that forces of the order of one dyne were required for a copper-copper contact of two single wires. Further, there seemed to be evidence of a change of state at the place of coherence, possibly orientation of the particles at the contact. In the present paper the authors follow the same method of investigation, adducing evidence that coherence can be explained, and only explained, by Lodge's original theory of fusion; and further establishing the after-effect, whether orientation or otherwise, mentioned in the former paper.

When electrical radiation falls on a contact of two wires, under suitable conditions coherence occurs. On applying a small measured force the cohored surfaces separate. On bringing them into contact again at the same places coherence will often, but not always, occur without the incidence of electric radiation. This can be repeated two or three times, but the power to cohere spontaneously soon vanishes. This spontaneous coherence is called recoherence. Like coherence, its presence is indicated by the forces required to sunder the surfaces. Several tables of these results are given.

Allowing that coherence itself is due to fusion, for which the evidence is abundant, recoherence may be due to (1) fusion, (2) molecular or intramolecular change, brought about during coherence by the locally violent surgings at the contact.

As to fusion, Prof. J. J. Thomson has suggested that the opposed spikes formed when the surfaces are torn asunder may be so fine as to be fused together by the small circuit current when the surfaces meet again. Without such spikes it is obvious the surfaces would be normal, and no spontaneous coherence could occur. Against the spike theory it is pointed out that recoherence never recurs more than a few times, which indicates some unstable condition of the surfaces. The orientation seen in magnetism can be destroyed by reversals of decreasing currents, by mechanical shock, and by heating. On adopting these methods to destroy recoherence, the authors obtained no definite results.

Recoherence is therefore still unexplained. Two surfaces can be pressed together with small but measurable forces by two methods:—(1) By a boom attached to a galvanometer suspension; a current in the galvanometer regulates the pressure between a wire on the boom and a fixed wire, these two forming the contact. (2) By a light balance of aluminium rendered only just stable; the pressure is regulated by a current in a solenoid, which acts on a magnet attached to one end of the balance. Both these methods are used by the authors to bring the surfaces into contact and to tear them apart again. The forces operating can easily be measured by a subsequent calibration.

Dr. W. WATSON, referring to the fact that when recoherence ceases to occur with a direct current it may be re-established by reversing the current, suggested that it might be due to the effect of the oscillations set up in the circuit at the make and break.

Dr. C. CHREE asked whether the authors could indicate approximately the relative number of cases in which recoherence failed when the current was not reversed, but

occurred when the current was reversed. He suggested that the fragmentary remains of the bridge which the authors described as existing during coherence might sometimes be so shaped as to make it easier for the current to pass in one direction than the other.

Prof. TROUTON asked if recoherence would occur without a current running through the contact. He suggested that one side of the contact might be a point and the other side approximately plane, so that the current would flow more easily in one direction than the other.

Mr. R. S. WHIPPLE asked if the effect depended upon the materials. In the case of a Callendar recorder, with a boom contact, the contact-pieces being made of platinum, it was found that the sensitiveness of the instrument depended upon the direction of the current.

Dr. R. S. CLAY asked if the reversal of the current which established recoherence took place when the substances were in contact.

Dr. P. E. SHAW, in reply to various questions, said that mere reversal of current would not produce the recoherence phenomenon. It only occurs as a sub-permanent effect following coherence, and cannot therefore be attributed to sparking caused by rapid reversals. As to the action of platinum and other materials as contact-surfaces, he found platinum singularly apt at coherence, but recoherence has not been looked for except in a copper-copper contact. Any explanation offered for recoherence must take account of the observed effects, viz., that it is a sub-permanent effect following coherence, is unstable to various influences, and arises most often by reversal of current but sometimes without such reversal.

NOTICES OF BOOKS

Refuse Disposal and Power Production. By W. FRANCIS GOODRICH. With Ninety-eight Illustrations. London: Archibald Constable and Co., Limited. 1904. Pp. 384.

It is only within recent years that the problem of refuse disposal has been tackled seriously and on the large scale. With the increase of sanitary knowledge it has been recognised that the old refuse heaps and pits on the outskirts of towns are admirably adapted for the incubation and, through the action of the wind, the dissemination of all kinds of harmful bacteria. Destruction by burning is the only practicable means for getting rid of this refuse, and though the strict sanitarian condemns the utilisation of the heat produced for the production of power, there can be no doubt that under some circumstance perfect cremation can be effected, and at the same time a great deal of otherwise waste heat utilised for driving such machinery as electric-lighting plant, pumps, &c.

It is true that in these days the commercial aspect of sanitary improvements is very prominent, and it may be that in some cases where the power cannot be utilised, and when it is a question of keeping down either the local council rate or the death-rate, it is the former that receives the greatest consideration, but, on the other hand, in many places that appears to be the last thing that enters into the minds of our local authorities. Still, when both can be done together, and of this the author feels confident, we cannot see any reason why it should not be attempted.

The author has treated the subject in a broad-minded manner, and he has placed sanitation in the forefront as the primary object of the destructor, and he looks upon it as a sanitary necessity, whether the power can be utilised or not.

The book is divided into twenty chapters, the early ones dealing with the old methods of refuse disposal. In Chapter V. we have British destructors described and illustrated, and Chapter VI. is devoted to the cost of labour. Chapters IX., X., and XI. are important ones, and deal with destructors combined with electricity works,

with sewage works, and with water works respectively. The latter combination we must condemn unhesitatingly. It is the constant endeavour of the water engineer, and of the chemist who advises him, to remove to the utmost all possible sources of pollution from the watershed, and we can hardly imagine anything more recklessly unwise than to deliberately cart town refuse into the close vicinity of reservoirs and filter beds day after day throughout the year, under such circumstances that the air must of necessity be loaded with dust, which is one of the most perfect microbe carriers.

Chapters XIII., XIV., and XV. discuss the comparative merits of different practical arrangements for complete combustion and satisfactory steam raising, while the re-remaining chapters deal with refuse destructors already in operation in London, in the rest of England, in Scotland, Ireland, Wales, and abroad.

There is an index of eight pages.

Fire and Explosion Risks. By Dr. VON SCHWARTZ. Translated from the Revised German Edition by CHARLES T. C. SALTER. London: Charles Griffin and Company, Ltd. 1904. Pp. 357.

This handbook deals with the detection, investigation, and prevention of dangers arising from fires and explosions of chemico-technical substances and establishments. It is intended for the use of fire insurance officials, fire-brigade officers, members of the legal profession, law officers, councillors, factory inspectors, and factory owners; and the chief endeavour of the author has been to insist on the indispensable aid that chemistry renders to the solution of the important problems arising in connection with the detection of the causes of accidental or premeditated outbreaks of fire.

The work is not designed to form an introduction to the variable practices of fire insurance companies, or a mere repetition of Trade Union regulations for the prevention of accidents, but to present to non-chemists a practical chemical tool, and to facilitate the investigation of the, to them, foreign domain of chemical technology in questions of fire risk and fire prevention.

The book is a large one, and is divided into eleven parts and fifty-nine chapters. The principal headings under which these parts are arranged are the various dangers of fire which may arise under different conditions. For instance, Part I. is on fires and explosions of a general character; Part II., dangers caused by sources of light and heat; Part III., dangers caused by gases; other parts deal with the dangers of various industrial materials, agricultural products, fats, oils, resins, petroleum, mineral oils, alcohols, ether, and other liquids; also dangers produced by metals, oxides, acids or salts, lightning, lighting materials, &c.

The author has dealt with the whole subject in a most comprehensive manner, and has given us a work which is worthy of the time and labour spent in its production. Besides a full table of contents there is a good index, so that any branch of the subject can be turned up in a short time.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., His Grace The Duke of Northumberland, K.G., President, in the Chair. Mr. Richard Bagot, Mr. W. Carrington, Mr. E. G. Fellows, Mr. W. R. Freeman, Mr. R. F. Nicholson, and the Hon. C. A. Parsons, F.R.S., were elected Members. The sincere thanks of the Members were returned to Dr. Andrew Carnegie, who is so intimately associated with the iron and steel industries, for his donation of £1200 to enable Prof. Dewar and Mr. R. A. Hadfield to prosecute their joint investigation on the Physical Properties of Steel and other Alloys at Low Temperatures, and to Dr. Frank McClean for his donation of £100 to the Research Fund of the Royal Institution.

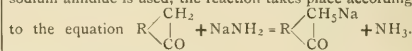
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 19, May 9, 1904.

Use of Alternating Currents in Chemistry, and Theory of the Reactions effected by them.—M. Berthelot.—The use of alternating currents in chemistry has been studied intermittently by several observers. The author summarises these researches, and discusses a theory of the action of such currents.

A New Method of Preparation of Alcoyl and Alcoylenic Derivatives of the Cyclic Ketones. Application to the Preparation of Alcoyl Menthones.—A. Haller.—When certain cyclic ketones are treated with sodium, a sodium derivative and the ketone of the corresponding alcohol is formed. If, instead of the metal itself, sodium amide is used, the reaction takes place according



Reactions of this nature can also be applied to the preparation of the alcoyl menthones.

Electric Osmosis in Methylic Alcohol.—A. Baudouin.—In methylic alcohol, as in water, the action of polyvalent ions is as follows:—A positive polyvalent ion (1) has little or no action on the charge of a positively charged substance in contact with the alcohol; (2) diminishes, and in certain cases reverses, the charge of a negatively charged substance. A negative polyvalent ion (1) has little or no influence on the charge of a negatively charged substance in contact; (2) diminishes, and in certain cases reverses, the charge on a positively charged substance.

Preparation of Samaria and Atomic Weight of Samarium.—G. Urbain and H. Lacombe.—(See p. 277).

Formation of Hydrogen Silicide by Direct Synthesis from the Elements.—Em. Vigouroux.—The author refers to a paper in *Comptes Rendus* of April 25, in which M. Violle gives an account of his preparation of hydrogen silicide direct from its elements. The author claims priority, and refers back to a paper of his own on July 18, 1901, in which he describes a preparation of hydrogen silicide direct from its elements.

Apparent Volatilisation of Silicon in Hydrogen.—A. Dufour.—In Geissler's tubes containing hydrogen arsenide the arsenic deposited by the discharge is displaced by simple distillation from the hot towards the cooler part of the tube whilst a current from the induction coil is traversing it. In tubes containing hydrogen silicide, the displacement of the silicon under the same conditions is explained by the formation of hydrogen silicide in the hot parts of the tube and its decomposition in Faraday's dark region. The volatilisation of the silicon is apparent only at this point.

A Property of Tin-aluminium Alloys.—Hector Pécheux.—When a little stick of either of the tin-aluminium alloys, Sn_2Al , Sn_3Al , Sn_2Al , SnAl_3 , whose surface has just been burnished, is plunged into cold water (at 13°) an abundant evolution of gas takes place round the polished part of the stick. The explanation of this is that, except at the tempered surface, the actual tin-aluminium alloy is not formed, but the metal consists of separate molecules of the two elements. Therefore a series of little thermo-electric elements exist of tin and aluminium, which decompose the water immediately. The tin and the aluminium, by reason of their very decided difference of specific heat ($\text{Al } 0.218 \text{ cal.}$, $\text{tin } 0.0562 \text{ cal.}$), are not at the same temperature (the molecules having been heated by the rubbing of the burnisher). An electromotive force is produced

which only ceases when the temperature of the two sets of molecules becomes equalised.

Differentiation of Primary, Secondary, and Tertiary Alcohols of the Fatty Series.—André Kling and Marcel Viard.—The authors have found a simple and rapid method of immediately concluding whether a given alcohol belongs to the primary, secondary, or tertiary group, by using the property of the unequal resistance of alcohols towards heat. Tertiary alcohols, if easily dehydrated with formation of non-saturated carbides, decompose into two molecules at the temperature of ebullition of naphthalene (218°), whilst the primary and secondary alcohols remain intact. If, however, the temperature is raised to 360°, the boiling-point of anthracene, the primary alcohols alone resist, both the secondary and tertiary ones being decomposed. If the vapour-density is taken by Meyer's method, first in the vapour of naphthalene, and then in the vapour of anthracene, it can at once be found, by the density determined, whether the alcohol is primary, secondary, or tertiary.

Formation of Chloroanilines.—Eyvind Bødtker.—During the preparation of aniline the author sometimes observed that the product of reduction of nitrobenzene by tin and hydrochloric acid is not always aniline alone. This body is accompanied by others boiling at a temperature above 180°. In two cases there was no aniline at all in the product. On distilling these other products with steam, large crystals are deposited on cooling, as well as an oil. These crystals, when re-crystallised from alcohol, fuse at 70°-5° and distil at 232°-3°. Analysis proves the product to have the formula $C_6H_5ClNH_2$, which is chloraniline, and the author believes the reaction to take place according to the equation $C_6H_5NO_2 + HCl + 2H_2 = C_6H_5\overset{Cl}{NH_2} + 2H_2O$.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 16.

Law of Thermic Constants, and the Heat of Formation of Compounds of Barium.—D. Tommasi.—Already inserted in full.

New Method for the Detection and Estimation of the Smallest Traces of Arsenic.—Armand Gautier.—Already inserted in full.

Estimation of Arsenic in Sea-water, Sea-salt, Rock-salt, Mineral Waters, &c., and in some Ordinary Reagents.—Armand Gautier.—Already inserted in full.

Purification of Sulphuretted Hydrogen for the Detection of Arsenic.—Armand Gautier.—Already inserted in full.

Action of Persulphate of Ammonia on the Metallic Oxides.—A. Seyewetz and P. Trawitz.—Already noticed.

Oxidation of Ammonia and of the Amines by Catalytic Action.—A. Trillat.—Already noticed.

The Nitration of Acetylgaïacol.—F. Reverdin and P. Crepieux.—The authors wished to see whether the toluene-*p*-sulphonic ether of gaïacol would give on nitration a product having a different constitution to that given by acetylgaïacol, and they repeated Barbier's experiment to form a nitroacetylgaïacol fusible at 135°-136°. By operating in the cold they obtained, not a nitroacetylated derivative, but a yellow body fusing at 122°, corresponding to the dinitrogaïacol of which the acetylated derivative fuses at 115°. By operating on the water-bath, they obtained the mononitroacetylgaïacol of Meldola, fusible at 101°. They repeated this nitration with various proportions of acetic and nitric acids, and with nitric acid of different density, and in every case they obtained the mononitroacetylated derivative fusible at 101°. An interesting conclusion is to be drawn from these experiments, viz., that the nitration of acetylgaïacol under the given conditions, and in the cold, gives rise to a de-acetylation and the formation of the dinitro-derivative, while, by

operating with heat, the acetyl resists, and the mononitro-acetylated derivative is formed.

Some Derivatives and Products of Condensation of β -Oxy- α -naphthoic Aldehyde.—A. Helbronner.—The author has continued his examination of β -oxy- α -naphthoic aldehyde, and has prepared the following derivatives:—Acetate of β -oxy- α -naphthoic aldehyde and benzoic ether; also other bodies, by its condensation with cyanacetate of ethyl and with acetylacetone.

Oxide of Ethylene from the β -Cyclohexanediol-1,2 and its Derivatives.—Leon Brunel.—Already noticed.

Action of Ammonia on the Oxide of Ethylene of the β - α -Cyclohexanediol.—Leon Brunel.—Already noticed.

Stachyose.—C. Tanret.—This is a long paper in which the author describes the preparation, constitution, and physical properties of stachyose, such as its solubility, rotatory power, and crystalline form. With the exception of their crystalline form, the author finds no difference between stachyose and mannetetose. On the other hand, M. Wyrouboff finds that their crystalline forms are identical, and that they are one and the same sugar, namely, a tetrose with the formula $C_4H_8O_{21}$.

Estimation of Essence of Turpentine from Landes.—M. Vèzes.—The author set himself a double problem—that of estimating the normal and the abnormal adulterants of essence of turpentine. The normal adulterants are oil of resin and colophane. The abnormal ones practically possible can be defined by two conditions—(1) They must be mixed with the essence without sensibly modifying its appearance; (2) their price must be lower than that of the essence. These two conditions are only fulfilled by a limited number of substances, namely, oil of petrole, white spirit or oil of schist, essence of petrole-ether, benzine, and sulphide of carbon. Methods for the detection and estimation of all these substances are given.

An Oxidising Bacterium: its Action on Alcohol and Glycerin.—R. Sazzerac.—While examining a wine vinegar the author obtained cultures which, after a short time, reduced the cupropotassic reagent. The microbial growth contained a microbe very different in form and in the appearance of its cultures from the *Mycoderma aceti* and the bacterium of sorbose. When carefully isolated on plates of glycerinated gelose at 2 per cent, it constantly gave, with glycerin broth, homogeneous cultures possessing this reducing power at ordinary temperatures. This microbe is fairly large, and is easily stained with the basic aniline colours, but not by Gram. It will not grow in meat broth, nor on potato, but grows well on glycerin gelose. The author has proved that it is capable of rapidly oxidising glycerin, transforming it into dioxycetone.

New Electric Accumulator.—D. Tommasi.—The novelty in this accumulator is in the form of the lead plates, which are designed to effect the circulation of the electrolyte and its diffusion through the active matter. An efficiency is claimed of 22 to 24 ampère-hours per kilogram of plates.

MISCELLANEOUS.

Bromides of Sulphur.—O. Ruff and G. Winterfeld.—With the object of settling the question of the existence of bromides of sulphur containing more bromine than S_2Br_2 , the authors, after having prepared this latter in a state of purity by heating the elements in a sealed tube to 100° and rectifying the product under reduced pressure, then mixed it with known quantities of pure bromine, and measured the fusion-points as well as the vapour tension of a large number of such mixtures. They have not succeeded in preparing double bromides related to SBr_4 , as takes place with SCl_4 . They come to the conclusion that bromides of sulphur, other than S_2Br_2 , do not exist.—*Berichte*, vol. xxxvi., p. 2437.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2325.

RADIO-ACTIVITY AND MATTER.

By CLEMENS WINKLER.

By the discovery of the phenomenon of radio-activity there has been opened up to physical, and presumably to chemical research also, a region which promises to surpass all our expectations in the peculiar and striking characteristics which it will reveal. We are confronted with a source of energy which seems to flow out continuously and spontaneously from itself, while we can only guess at its origin; with manifestations of energy which do not resemble those already known either in character or mode of expression; with substances which are like the elements in all particulars, and yet seem to possess a new nature. The most typical of these substances is radium, which in the opinion of its discoverer (*cf.* M^{me}. S. Curie, "Untersuchungen über die Radio-activen Substanzen," Uebersetzt und mit Literatur, Ergänzungen Verschen, von W. Kaufmann, Braunschweig, 1904, S. 2) is to be regarded from a chemical point of view as a new element, and by its inclusion in the Atomic Weight Table of 1904 of the International Atomic Weight Committee is recognised as such.

Far less is definitely known about the other radio-active substances which have been discovered. The existence of polonium, discovered by P. and S. Curie (*Comptes Rendus*, vol. cxxvii., p. 175; *Chem. Centralbl.*, 1898, ii., 572) was for a long time regarded by many as doubtful, but it appears to have been revived in W. Marckwald's radio-tellurium (*Berichte*, 1902, xxxv., 2283 and 4239; 1903, xxxvi., 2662). Investigations which are certainly comprehensive and specially remarkable for the chemical work involved in them have been performed with radio-lead (K. A. Hofmann and E. Strauss, *Berichte*, 1900, xxxiii., 3126; 1901, xxxiv., 8, 907, 3033, 3970; K. A. Hofmann, A. Korn, and E. Strauss, *Berichte*, 1901, xxxiv., 407; K. A. Hofmann and V. Wolff, *Berichte*, 1902, xxxv., 1453; 1903, xxxvi., 1040); but without taking into account F. Giesel's objections raised against them (*Berichte*, 1900, xxxiii., 3569; 1901, xxxiv., 3772) they have up to the present not been so far successful as to entitle us to regard it with absolute certainty as a new element. Again, the same might be said of A. Debiere's actinium (*Comptes Rendus*, vol. cxxix., p. 593; vol. cxxx., p. 906; *Chem. Centralbl.*, 1899, II., 1003; 1900, I., 1059), and of other radio-active substances such as have been supposed to have been discovered, for example, in the earths of the cerium and yttrium group (K. A. Hofmann and E. Strauss, *Berichte*, 1900, xxxiii., 3126; F. Giesel, *Berichte*, 1903, xxxvi., 342).

This uncertainty is quite explicable if we consider that for the performance of all researches up to the present at the most only very small quantities of pure or even enriched substance have been at the disposal of the investigators, for which reason the study of their properties, specially of those to be regarded as chemical, has been rendered much more difficult. Moreover, the study of the chemical behaviour of the substances in question naturally became of secondary importance, because of the great incentive to research which was given by the examination of the mysterious phenomenon of radio-activity with the use of the photographic plate, the electroscope, and phosphorescence screen, and if it has been by no means neglected it has certainly not received the attention that is usually paid to it when the characteristic nature of newly discovered elements is being established.

It has been found that the working up of the raw material containing radium may be performed by a method which is

very simple in itself, and in essentials follows the method of preparation of barium. In this method, by making use of certain differences of solubility, the method of fractionation has been successfully employed, and we have thus become acquainted with a characteristic radium spectrum. What importance, however, is to be ascribed to the spectral reaction is a question which, for the present, must remain undecided. In the case of a substance which has been separated from the very complex material of the Joachimsthal residues, and then only in exceedingly small quantities, it is quite possible that the spectral reaction might prove to be misleading. Apparently there exists little agreement between the spark spectrum of radium described by Demarcay (*cf.* S. Curie, *loc. cit.*, p. 20) and the flame spectrum described by F. Giesel (*Berichte*, 1902, xxxv., 3608), and the orange-red lines in the spectrum of radium bromide as well as the red colouration which this salt imparts to the flame may possibly be due to a foreign residue of the metals of the alkaline earths. Moreover, no compounds of radium have been sufficiently accurately examined, nor do we know of definite reactions peculiar to it. Strictly speaking, the only positive evidence in favour of its promotion to the position of a separate element is afforded by the determination of its atomic weight, which is so high as to justify the conclusion that radium, taking into account its similarity to barium, forms a new member of the metals of the group of the alkaline earths.

Radium-lead has been chemically more thoroughly examined than radium, without any considerable difference between its reactions and those of ordinary lead being detected. It was thought that in its atomic weight also a decided divergence had been obtained (K. A. Hofmann and E. Strauss, *Berichte*, 1901, xxxiv., 8, 907). The determination of the atomic weight of radio-lead was made by ascertaining the amount of sulphuric acid in the sulphate. The amount of SO₂ in the sulphate was fixed at 41.35 per cent, while that of lead sulphate only amounts to 31.71 per cent.

From this result, assuming that radio-lead, like thorium and uranium, is tetravalent, it was calculated that its atomic weight is 260.2, while that of lead is only 206.9. The correctness of the determination seems, however, doubtful because the sulphate with which it was carried out, after driving off the excess of sulphuric acid, was not heated until it began to glow, but was only dried at 400–420°. At such a low temperature experience has proved that it is not possible to expel completely the free acid which adheres to it, and thus it is not surprising to find the sulphuric acid of the sulphate examined higher than that of lead sulphate. The atomic weight of radio-lead cannot of course be deduced from it, and also the supposition, founded on the results of other sulphuric acid determinations which were affected by the same error, that possibly the homologue of manganese (the long sought ekamanganese of Mendeleeff) and of tin had been discovered, falls to the ground.

The researches, so admirable in all other respects, on the radio-activity of substances cannot, generally speaking, be regarded from a chemical point of view as adequate. Even the results of fractionation are to be accepted with circumspection, because they may easily give rise to fallacies. When the discovery of spectral analysis threw the world into a state of agitation similar to that now excited by the discovery of radio-activity, it was believed in all seriousness that calcium had been decomposed, because it had been found possible to cause the disappearance of the green line of its spectrum in one of the parts obtained by fractional precipitation of a solution of calcium chloride, and in connection with this crystallographers even began to make observations on the striking multiplicity of the calc spar form. Similar and certainly pardonable errors could occur in other cases, so that it can by no means be definitely stated that this has actually happened in the fractional treatment of radio-active substances.

It may now be asked whether it is generally established that the presence of a new element in a substance may be

presumed simply from the fact that it is radio-active. It would then be very remarkable if every one of the numerous elements, long known themselves, in which radio-activity has been observed, possessed a new attendant, also to be regarded as elementary, of practically perfect similarity of chemical behaviour. Many arguments may be brought forward against such an assumption quite apart from the fact that it is contrary to the present conception, which is not yet destroyed, regarding the nature of the elements, as well as to all experience. Uranium, an element undoubtedly to be regarded as typical in such a case, according to Sir William Crookes (*Proc. Roy. Soc.*, lxi., 409; *Chem. Centrbl.*, 1900, II., 364), may be decomposed into an active and an inactive part simply by treatment of its hydrous nitrate with ether, or by fractional crystallisation or fractional decomposition of the same compound by heating without either part showing the least difference from the other as regards its chemical behaviour. Béla v. Lengyel (*Berichte*, 1900, xxxiii., 1237), who expressed doubts as to the existence of radium, made barium active by heating its nitrate with uranyl nitrate, and Henri Becquerel (*Comptes Rendus*, cxxxi., 137; *Chem. Centrbl.*, 1900, II., 422), by precipitation with sulphuric acid of a solution of barium chloride to which active uranyl chloride had been added, prepared a strongly active barium sulphate, while the activity of the uranium experienced simultaneous diminution. Also K. A. Hofmann and E. Strauss (*Berichte*, 1900, xxxiii., 3126; 1902, xxxv., 1453) have obtained inactive fractions from active uranium compounds; on the other hand, they have succeeded in completely withdrawing the activity from uranium by means of barium or bismuth compounds. But the experiments of A. Debiere (*Comptes Rendus*, cxxxi., 333; *Chem. Centrbl.*, 1900, II., 557) are specially noteworthy; they were carried out by a similar method, but actinium was used, and by means of them it was shown that it was easily possible to make the compounds of barium active in such a way that they could scarcely be distinguished from those of radium, except for the fact that they gave no radium spectrum, and showed a decrease of activity after a time. The barium which has been made active is said to stand between barium and radium as regards its properties. Its chloride, like that of radium, is self-luminous when anhydrous, and also by fractional crystallisation may be decomposed into a more active and a less active part.

Only by induction can such striking observations be explained. Also the objection to Béla v. Lengyel raised by F. Giesel (*Berichte*, 1900, xxxiii., 1665), that the activity of the barium first caused by this may be produced by the radium contained in the uranium salt used, was quashed, because, as has been described, the same result has been obtained under other conditions, and also on a far large scale.

And what is to be said regarding the supposed material emanation of radio-active "elements," their instability, their decomposition with splitting off of helium, and the decomposition of the elements themselves? So far no proof has been furnished that elements of high atomic weight, among which gold and platinum are to be reckoned, are polymers of elements of low atomic weight, and that they could be decomposed into the latter. The conception of an element still retains its former meaning, and quite different and more thorough chemical experiments would be necessary to destroy it. But it appears every day more plainly that radio-activity seems to be extraordinarily widely diffused, and this idea leads to the question whether it may not be a purely physical process, a phenomenon which may adhere to matter without influencing its chemical composition something like the magnetism of magnetic iron ore, which, like it, may be increased, transferred, apparently annihilated, and again produced, and which also shows itself as a mysterious expression of energy proceeding from the substance, though nobody imagines that in magnetic ferro-ferrous oxide the presence of another element is to be assumed different from that in non-magnetic iron oxide. The idea of material difference will not occur to anybody,

since Fr. Heusler (*Schriften d. Gesellsch. z. Beförd. d. Gesammt. Naturwissenschaften z. Marburg*, 1904, xiii., 255; and *Zeit. für Angew. Chem.*, 1904, 260) succeeded in preparing alloys capable of magnetisation from non-magnetic metals such as manganese, tin, antimony, and aluminium. As regards radio-activity also we should be independent of the assumption of a material difference if the statement of F. Richarz and Rudolf Schenck (*Sitzungsber. d. Königl. Preuss. Akademie d. Wissenschaften*, 1903, lii.; 1904, ii.) remained without valid objection, viz., that oxygen on ozonisation becomes radio-active in such a way that it acts upon the photographic plate, causes intense luminescence of Sidot's blende (but not of other substances), and like radium gives rise to development of heat.

Considering the excitement about radium which now pervades the world, and makes itself felt to no small degree in lay circles, it is rather galling for chemists that they cannot say more about radium, which was discovered almost six years ago, than that it is exactly like barium except that it has a higher atomic weight, and possesses the wonderful spontaneous radiation. The chemical nature of radium is as yet almost unknown, and yet questions are often put about it, especially in those places in which pitchblende has been discovered, and where people are already dreaming of a most promising "radium mining" and a future "radium industry." So far as is yet known the occurrence of radio-active substances is entirely bound up with that of uranium. This is striking in the highest degree and cannot be explained if we are to assume the presence of special elements in these substances. For if the occurrence together of certain fundamental substances is by no means extraordinary and can be explained from their position in the system, their valence, the isomorphism of their compounds, and other similar characteristics, yet we never meet with the exclusive occurrence together of any substances, as would appear to be the case here. Thorium is, perhaps, an exception, or at any rate G. F. Barker (*Chem. Zeit.*, 1903, 522) ascribes to this element a radio-activity independent of the simultaneous occurrence of uranium. K. A. Hofmann and F. Zerban (*Berichte*, 1902, xxxv., 531; 1903, xxxvi., 3093) are of the contrary opinion, and F. Zerban (*Berichte*, 1903, xxxvi., 3911) also thinks that he has proved the presence of a small quantity of uranium in monazite sand, which has hitherto been supposed to be free from uranium. However, objection may be made to the method of research used by him, which originated with Laube (*Zeit. für Angew. Chem.*, 1889, 575), and was meant originally, not for analytical purposes, but for the working up of uranium residues.

The material for obtaining radium and other radio-active substances has hitherto been chiefly furnished by the residue obtained during the working of pitchblende for uranium preparations at the K. K. Österreich-Uranfabrik in Joachimsthal. This residue remains on solution in dilute sulphuric acid of pitchblende which has been previously roasted, ignited with soda and saltpetre, and washed with water. It consists essentially of gangue, silicic acid, iron oxide, basic iron sulphate, and lead sulphate, but also contains some bismuth and silver. Its weight amounts to 40 per cent of the weight of the uranium ore worked up, and it may be estimated that during the fifty years the Joachimsthal Uranfabrik has existed 150–200 tons of this residue have been made. The total amount of radio-active substances contained in it is difficult to estimate, but it would amount to a few grms. only of radium and to fractions of a gm. of radio-tellurium.

The residue in question possesses 4 to 5 times the activity of metallic uranium. 1000 kilograms of it, according to S. Curie, yielded 10–20 kilograms of raw sulphate of 30–60 times the activity of uranium, and this again gave 8 kilograms of barium chloride containing radium with activity 60 times that of uranium. From this it seems to follow that the increase of activity does not keep pace with the enriching of the barium compounds, but falls far short of it. Thus it does not seem to form a trustworthy

standard for the increase of the amount of radium present. Even a chloride brought by fractional crystallisation to 3500 times the activity of uranium must have consisted essentially of barium chloride, as the atomic weight of the metal contained in it amounted only to 140 and was thus not much higher than that of barium. No information is at hand concerning the activity of the presumably purest radium chloride, which still, however, contains some barium, but the best radium preparations are said to be 50,000 to 100,000 times more active than uranium (O. Dammer, *Handb. d. Anorg. Chemie*,¹ vol. iv, p. 952).

A question of great importance is: In what form of combination is the radium contained in pitchblende and in the residue resulting on its solution? In the latter case most decidedly as sulphate, and probably also in the former, because heavy spar ordinarily accompanies pitchblende. As now the solubility of the sulphates of the metals of the alkaline earths decreases with rise of atomic weight, radium, as the last member of the group, must form the least soluble sulphate. Hence, and from the isomorphism of the barium and radium compounds (F. Rinne, *Centralbl. f. Min. u. Geol.*, 1903, 134), it must be concluded that the heavy spar accompanying pitchblende is the real carrier of the radium contained in the Joachimsthal ore. But Sir William Crookes (*Proc. Roy. Soc.*, lxxi, 409; *Chem. Centralbl.*, 1900, II., 364) has not succeeded in proving the existence of radio-activity in any of the heavy spar specimens examined by him, and, even if amongst them that from Joachimsthal was not included, this is strange, inasmuch as according to all experience relating to the occurrence together and mutual substitution of the elements, it is not to be assumed that radium, unlike calcium and strontium, is excluded from appearance in natural barium compounds, if it stands beside barium actually as an independent element. But if heavy spar containing radium exists, the radium it contains will pass over into the barium chloride prepared artificially from it, and then even if it were ever so small in quantity it could not be difficult to concentrate it by fractional crystallisation of this salt on a large scale. The experiment with 50 kilograms of commercial barium chloride planned for this purpose by S. Curie has only given negative results.

But even if radium for some unknown reason can only occur with uranium it must, at any rate in the Erzgebirg, be found comparatively widely distributed. For besides the actual places in which pitchblende has been found, like Joachimsthal or those at present more or less worked out, e.g., Johanngeorgenstadt, Schneeberg, Annaberg, and Freiberg, we find in the region named above rock containing very little uranium, particularly granite, in which the presence of uranium may be shown by a small quantity of uranite and uranocircite, which acts on the photographic plate, and sometimes also is visible in the paving material of roads. Hence it seems that it may not be impossible to discover, in that region in which the occurrence of bismuth is very widely extended, raw materials which may be successfully worked for radio-active substances. By the preparation of these latter pure in larger quantities and their thorough chemical examination we shall perhaps succeed not only in approaching some explanation of the nature of radio-activity, but also in establishing without any doubt the existence of radio-active elements of special nature and definite chemical behaviour.

Use of Berthelot's Calorimetric Bomb to prove the Existence of Arsenic in the Organism.—Gabriel Bertrand.—M. Berthelot has already used his calorimetric bomb for the estimation of various simple bodies present in organic matters. The author has applied this method, with great success, to the detection of traces of arsenic. In this paper he describes the details of the method he has employed, as well as other experiments on the limit of sensibility, control experiments, &c. He finds that arsenic is present normally in the shell of the turtle, in sponge, the white of egg, the thyroid gland, and other substances.—*Bull. Soc. Chim.*, Series 3, xxix., Nos. 18—19.

REPORT ON THE DETERMINATION OF NITROGEN.*

By F. W. MORSE.

(Concluded from p. 284).

Comments of Analysts.

Department of Foods and Feeding, Hatch Experiment Station.—Mechanical conditions were not uniform; a considerable portion of each sample was coarse. The substances should be reduced so as to pass a sieve of No. 2 perforated sheet metal (40 perforations to the square inch). This is especially true of mixtures containing highly nitrogenous foods; otherwise sampling for nitrogen determinations or availability, where only a small amount is employed, is very unsatisfactory, and concordant results are practically impossible except by chance.

In the determination of total nitrogen, by the plain Kjeldahl method, the reagents used in the digestion were one-half gm. re-sublimated metallic mercury (B. and A.), 25 c.c. chemically pure sulphuric acid, specific gravity 1.84 (B. and A.); and, in the distillation, 200 c.c. distilled water, 25 c.c. potassium sulphide solution, 1—25 (Merck), 100 c.c. sodium hydrate solution, 1—2 ("Red heart"), one-half gm. granulated zinc (30 mesh, B. and A.).

In the determination of total nitrogen by the plain Kjeldahl method plus sulphate, the reagents used were the same as in the plain Kjeldahl with the addition of 10—12 grms. of crystallised potassium sulphate (B. and A.) to facilitate the digestion and to insure perfect oxidation.

The results were as follows:—

1. More perfect oxidation; this is noticeable in every case where cotton-seed meal is present; the average increase in nitrogen for the samples is 0.056 per cent, 3.943 per cent, and 3.887 per cent.

2. More rapid oxidation; the solutions cleared—i.e., bulk of organic matter was destroyed in twenty-one minutes (average) as against forty-one minutes in the plain Kjeldahl method.

3. There is less reaction upon the addition of water in preparing for the distillation than in the case of the plain Kjeldahl method.

The mechanical condition prevented the obtaining of closely agreeing results in both methods.

The neutral permanganate solution was prepared from pure crystallised reagent (Merck). The plain Kjeldahl method plus sulphate was used for the determination of the nitrogen in the insoluble residue. Unevenness of the samples and variation in action of the solvents probably account for the poor parallels. The objectionable features in the manipulation of this method are chances of error from repeated transferring, &c., length of time required, and difficult filtration.

The alkaline permanganate solution was prepared from pure crystallised potassium permanganate (Merck) and stick sodium hydrate, purified by alcohol (Merck). The results are apparently low. This can be accounted for, partly at least, by errors in the method as sent out:—

1. A weak, incorrectly prepared solution. Sixteen grms. of powdered crystallised potassium permanganate and 150 grms. of sodium hydrate should be dissolved in water, and after cooling made up to 1000 c.c.

2. Substances too coarse to receive the maximum effect of the solution.

3. Digestion too short. The heating should be maintained for one hour without distilling over, but not necessarily below ebullition, and the flask should be shaken occasionally to wash down adhering particles. The distillation should be conducted as usual, simply using care not to break the flask. The objectionable feature in the manipulation is the adhering of the material to the sides of the flask and the smallness of the solution with which to wash it down. Little or no frothing occurs after proper

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

digestion (see the "Fourteenth Report of the Vermont Experiment Station," p. 219).

C. H. Jones, Vermont.—The filtrate after the digestion with neutral permanganate solution was colourless in each case.

With the alkaline permanganate method I am satisfied that the preliminary digestion of thirty minutes or one hour is necessary, not so much that the results may be slightly increased, but that danger from frothing is lessened if not entirely obviated when the distillation begins. It should be noted that it is quite necessary to rotate the flask occasionally during the digestion and distillation if the material shows a tendency to creep up the sides of the flask.

I re-ground Samples 1, 3, and 4 before making any tests, as the samples containing blood seemed to me too coarse to enable one to get concordant results with the Kjeldahl method.

Y. B. Robb, Maryland.—The total nitrogen was determined by the Gunning method, and the samples were digested for one hour.

In the alkaline permanganate method the flasks were shaken several times during the process of distillation to prevent the material adhering to the sides of the flask.

In my opinion the neutral permanganate method is very unsatisfactory, as the results obtained by it are not at all concordant.

F. W. Woll, Wisconsin.—No. 597, S. and S. filters 9 c.m. were used.

Sample No. 1, blood, washed clear.

Sample No. 2, cotton-seed meal, washed turbid, which necessitated re-filtering through double paper (No. 597, S. and S.).

Sample No. 3, washed clear.

Sample No. 4, washed turbid, treated the same as sample No. 2.

Jena 800 c.c. round-bottom flasks were used for distillation.

A. M. Peter, Kentucky.—It being apparent that all the permanganate was reduced before the digestion was completed in the alkaline method, an additional quantity of 1.6 grms. permanganate dissolved in 100 c.c. water were added to each of the flasks in set 3, and the distillation repeated, the following additional quantities of nitrogen being obtained:—Sample No. 1, 1.25 per cent; No. 2, 1.30 per cent; No. 3, 1.54 per cent; No. 4, 1.40 per cent. At the close of the distillation the liquid in the flasks was still green from excess of permanganate.

Another portion of 1.6 gm. permanganate and 100 c.c. water was added to each flask, and the distillation was repeated with the following results:—Additional nitrogen obtained from sample No. 1, 0.40 per cent; No. 2, 0.20 per cent; No. 3, 0.20 per cent; No. 4, 0.13 per cent.

The total available nitrogen obtained in these three distillations was as follows:—Sample No. 1, 3.22 per cent; No. 2, 2.76 per cent; No. 3, 3.03 per cent; No. 4, 3.01 per cent.

Another set of determinations was made, following the referee's directions in every respect, except that 200 c.c. of alkaline permanganate were used instead of 100 c.c. The results were that the following percentages of available nitrogen were obtained:—Sample No. 1, 2.24; No. 2, 1.90; No. 3, 2.17; No. 4, 2.10.

Still another series was made, following the referee's directions in every particular, except that the distillation was pushed until the residues in the flasks were dry at the bottom. In this set some parts of the residue may have been overheated, as the flasks were over the direct flame. The results were the following percentages of available nitrogen:—Sample No. 1, 2.58; No. 2, 2.16; No. 3, 2.93; No. 4, 1.50.

It appears that there is not enough permanganate in 100 c.c. of the alkaline solution as prescribed to complete the decomposition. I do not see that either method is giving us available nitrogen, and the alkaline permanganate, as carried out, seems to be especially faulty.

Discussion of Results.

Without discarding any figures on total nitrogen, the differences between maximum and minimum results are, respectively, 0.60 in No. 1, 0.46 in No. 2, 0.36 in No. 3, and 0.40 in No. 4. These discrepancies are large for total nitrogen.

The point mentioned by the referee last year with regard to the time of digestion is brought out here, namely, that the digestion should be prolonged in order to insure the recovery of all the nitrogen.

Setting aside the highest and lowest results, we have determinations ranging within less than 0.3 per cent, which is as exact a result as has been obtained in the past.

When the results on the availability of the nitrogen are considered, it is seen that duplicate analyses by any one analyst agree well, taking each method by itself.

Both methods have been evolved from the method of determining albumenoid ammonia in water, as is shown by the first method proposed in the reports of the Association (U.S. Department of Agriculture, Division of Chemistry, *Bulletin*, 47). They differ radically in principle, the neutral permanganate being used merely to dissolve the nitrogen, while the alkaline method dissolves it, and also transforms it into ammonia.

The critical features of the former method are time and temperature, as in determining citrate soluble phosphoric acid. The latter method possesses the same weakness possessed by Wanklyn's method for albumenoid ammonia—that in the case of vegetable matter it will recover only about one-half of the total nitrogen, and its critical features are the amount of permanganate which will be affected by cellulose and the amount of distillate which is collected.

As is mentioned by Mr. Peter, neither method seems to give the available nitrogen; yet I can think of nothing better. We have in fertilisers about all forms of vegetable and animal proteids, both raw and cooked. Obviously none of the usual solvents for proteids can be employed in this work. We must therefore attempt to use a substitute.

The neutral permanganate method has compared most favourably with vegetation tests in its relative effects on the various nitrogenous fertilisers. On the other hand, the alkaline method is a convenient one for determining whether a fertiliser is easily transformed to ammonia or not.

This method needs to be modified somewhat. If more time had been available, the referee would have tried increasing the amount of solution used in order to have a greater volume for distillation and the regulation of the amount of distillate collected. Reasoning from the practice with albumenoid ammonia in water analysis, this latter point would be especially important. Another fact which bears on this point is that in residues after distillation, when washed as in the neutral method and the insoluble nitrogen determined, the nitrogen was found to have been almost totally dissolved, even in a sample of ground leather.

With regard to the neutral method I think that the use of a Witt plate or Hirsh funnel is, as a rule, advantageous in reducing the time and enabling one to use a smaller filter-paper.

I do not think it necessary to make a change in the method of determining total nitrogen, although the weight of evidence is in favour of prolonging digestion for three or more hours. The increase in nitrogen is so slight that it would be negligible in some work, while important in others. The good sense of our station chemists will result in their familiarising themselves with the work of the Association on such a point, after which the character of the work will govern the mode of execution.

I believe that the alkaline permanganate method is worthy of further attention, and that each method should be reduced to a form which will give more closely concordant results.

My only recommendation as a result of this year's work is that the subject be continued by the next referee, with the view of getting more concordant results with each method.

BASIC CHLORIDE OF COPPER.

By ANDRÉ BROCHET.

THE crystallised basic copper chloride, $\text{Cu}(\text{ClO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$, has been obtained by M. Bourgeois (*Bull. Soc. Chim.*, [3], vol. xix., p. 948) by decomposing chlorate of copper by heat. During my recent researches I have observed that this basic salt is obtained in the amorphous state under the same conditions as the basic chloride, either by the action of an alkaline or an alkaline-earthly base on the chlorate of copper in solution, or by the action of the hydrate of copper on an excess of chlorate in solution. All these reactions take place as well in the cold as when heated.

The dried product forms a greenish-blue powder analogous to the corresponding basic salts. It answers to the formula given by M. Bourgeois; however, it always contains an excess of hydrate of copper and a certain quantity of water, which cannot be got rid of, either by heating to 100° or in *vacuo*.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 6.

THE ELECTROLYSIS OF ALKALINE AND ALKALINE-EARTHY CHLORATES WITH AN ANODE OF COPPER.

By ANDRÉ BROCHET.

MESSRS. Bancroft and Burrows have described the curious phenomena which take place when chlorate of potassium is electrolysed with an anode of copper. In a previous paper on this subject, I have given, for my own part, some explanation of these occurrences. I have extended this research to the more soluble chlorates of sodium and barium; barium has the further advantage of being easily detected and estimated in the precipitate.

Knowing the action of chloric acid, and of chlorate of copper on this metal, it is easy to complete this explanation. I have already stated that the anion, ClO_3 , is decomposed on contact with the copper anode, and thus permits the attack of a greater quantity of the metal. This is due to a purely chemical action apart from the electrolytic one.

Now, in the case of the alkaline and alkaline-earthly chlorates and of chlorate of copper, this solution cannot be more than double the amount of copper precipitated on the cathode of the voltameter.

The manner in which the electrolysis of chloric acid and of chlorate of copper goes on, has led me to modify my first hypothesis and to admit that the decomposition of the ion, ClO_3 , or of the chlorate of copper on contact with the anode, instead of being the principal cause of the attack of this anode, was the consequence of it.

The reaction which takes place is due simply to the fact that the copper goes into solution in the form of cuprous ions, but, as in certain electrolytes, cyanide of potassium, for example, the metal simply dissolves in the form of cuprous ions, and remains as such, in the present case the copper is dissolved in the form of cupric ions; further, the cuprous salts formed by the primary action, the chloride or the oxide, are more or less rapidly oxidised.

According to the conditions of temperature, density of current, concentration, &c., the amount of cupric salt formed primarily is more or less considerable, which explains why the ratio of the copper dissolved at the anode to the copper precipitated on the cathode of the voltameter is variable and hardly equal to 2.

It is not necessary here to give in detail the experiments made under the same conditions as those of Burrows, and which have given me analogous results. In a general manner, whether we have to do with the acid, with chlorate of copper, or with an alkaline or an alkaline-earthly chlorate, the reaction at the anode is the same.

In the case of the acid, the products formed pass into solution; with the salt of copper, they are found in the

form of double salts; with the alkaline or alkaline-earthly chlorates, the basic salts are partially decomposed by the alkali formed at the cathode, but the decomposition is not complete, and there remains in the precipitate of the chloride and of the chlorate a state of equilibrium with the alkali remaining in solution. The hydrogen at the cathode thus goes first to the chlorate, so that the precipitate will not contain any, then to the oxide to form metallic copper insoluble in dilute sulphuric acid, and soluble in hot concentrated acid with the evolution of sulphurous acid gas. For the above mentioned reasons the amount of copper contained in the precipitate will be less than that obtained in an analogous precipitate from a salt unable itself to furnish any element reducible by hydrogen, such as sulphate of sodium, for example.

Thus the black precipitate is very impure; in fact, it contains, besides the oxide of copper, metallic copper, chlorides, and the alkali corresponding to the salt electrolysed, as is easy to prove by using chlorate of barium.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 6.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, June 2nd, 1904.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MESSRS. T. L. D. Porter and C. Smith were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Herbert Dalton, 85, Hayter Road, Brixton Hill, S.W.; John Evans, 67, Surrey Street, Sheffield; Archie Willoughby Hensell, Witton Hall Industrial School, Birmingham; Arnold Bertram Tonkin, Durban, Natal; Henry Bridges Weeks, The Retreat, Infield Park, Barrow-in-Furness.

Of the following papers, those marked * were read.

*95. "Imino-ethers and Allied Compounds corresponding with the Substituted Oxamic Esters." By GEORGE DRUCE LANDER.

When piperidine and phenylhydrazine condense in anhydrous media with methyl dichloro-oxalate, the dipiperidide, $\text{CO}_2\text{Me} \cdot \text{C}(\text{C}_6\text{H}_{10})_2 \cdot \text{OMe}$, and the imino-compound, $\text{CO}_2\text{Me} \cdot \text{C}(\text{OMe}) \cdot \text{N} \cdot \text{NHPh}$ (m. p. $123-124^\circ$), result, as described by Anschütz and Stiepel (*Annalen*, 1899, cccvi., 11). The latter substance gives the corresponding acid, which is unstable, yielding, on boiling with aqueous methyl alcohol, carbon dioxide, oxalic acid, and formazan.

With aniline and *p*-toluidine it was not found possible to isolate either the mixed ortho-compounds, $\text{CO}_2\text{Me} \cdot \text{C}(\text{NHR})_2 \cdot \text{OMe}$, or the imino-ethers, $\text{CO}_2\text{Me} \cdot \text{C}(\text{NR}) \cdot \text{OMe}$ of Anschütz and Stiepel. Diarylamidino-oxalic esters, $\text{CO}_2\text{Me} \cdot \text{C}(\text{NR}) \cdot \text{NHR}$, and small quantities of the corresponding amidinoamides were obtained in the cold, and also in boiling xylene solution, together with substituted oxamates and oxamides, substituted formamides, carbon dioxide, and methyl chloride.

Semi-N-phenylimidino-oxalic dimethyl ether—

$\text{CO}_2\text{Me} \cdot \text{C}(\text{NPh}) \cdot \text{OMe}$,

a liquid (b. p. $130-132^\circ/12$ m.m.) prepared by methylating methyl oxalinate by means of silver oxide, resembles the diethyl analogue (*Trans.*, 1901, lxxix., 699). Dry ammonia was found to be without action in the cold on any of the oxalimino-ethers.

The following compounds were described:—*Methyl phenylimethyloxamate* (b. p. $170-175^\circ/13$ m.m.); *semi-N-tolylimidino-oxalic diethyl ether* (b. p. $160^\circ/14$ m.m.); *methyl-p-diphenylimidino-oxalate* (m. p. $65-66^\circ$), and the analogous *di-p-tolyl methyl ester* (m. p. 103°), and *ethyl ester* (m. p. $98-100^\circ$).

The diphenyl- and di-*p*-tolyl-amido-oxalic acids lose carbon dioxide on heating, and change into substituted formamidines,—



whilst the di-*p*-tolylamidino-ester, on heating, evolves carbon dioxide and yields di-*p*-tolylmethylformamidino. The hydrochlorides of the amidino-esters decompose on fusion, giving rise to methyl chloride, carbon dioxide, and formamidines.

Methyl iodide and the di-*p*-tolylamidino-ester give the methyl ester, $\text{CO}_2\text{Me}\cdot\text{C}(\text{N}(\text{C}_6\text{H}_5)_2)\cdot\text{NMe}\cdot\text{C}_7\text{H}_7$ (m. p. $91-92^\circ$), the corresponding acid decomposing at $80-81^\circ$ into carbon dioxide and the foregoing di-*p*-tolylmethylformamidino.

*96. "The Action of Heat on α -Hydroxycarboxylic Acids. Part I. α -Hydroxystearic Acid." By HENRI RONDEL LE SUEUR.

The investigation of the action of heat on α -hydroxystearic acid, briefly described in a preliminary note (*Proc.*, 1904, xix., 14), has now been completed, and in view of the fact that Blaise (*Comptes Rendus*, 1904, cxxviii., 697) has recently published an account of work of a similar nature, it appears desirable to set forth the results of this investigation.

Margaric aldehyde, $\text{C}_{16}\text{H}_{33}\cdot\text{CHO}$, produced on heating α -hydroxystearic acid, crystallises in needles, and melts at 36° ; its oxime and semicarbazone melt at 89.5 and $107-108^\circ$ respectively. With hydrogen cyanide, it forms α -hydroxyheptadecyl cyanide (m. p. $61.5-62.5^\circ$), which, on partial hydrolysis, gives α -hydroxystearamide melting at $148-149^\circ$, and, on complete hydrolysis, α -hydroxystearic acid.

Margaric acid, obtained by oxidation of the above aldehyde with potassium permanganate, melts at $60-61^\circ$; its methyl and ethyl esters melt at 29° and 28° respectively. α -Bromomargaric acid crystallises from dilute acetic acid in glistening plates (m. p. 52.5°).

DISCUSSION.

Dr. LEWKOWITZ pointed out with regard to the α - and β -hydroxystearic acids obtained from oleic and isoleic acids respectively that the α -compound was not identical with the α -acid described by the author, since, on oxidation with chromic acid, it yielded sebacic and ketostearic acids, and was probably a κ -acid. It would be of interest to know whether the author's margaric acid was identical with Kraft's margaric acid or with daturic acid; the latter might now be regarded as an acid which could be somewhat easily obtained, since it had been found in lard as the mixed glyceride, daturidistearin.

Dr. LE SUEUR, in reply, said that the acid which he had described was probably identical with Kraft's margaric acid, as the two substances melted at practically the same temperature; but, as Kraft had not prepared any characteristic derivatives from this acid, he could not state definitely that they were one and the same substance. These remarks also applied to daturic acid, which melts at 55° .

*97. "Ionisation and Chemical Combination." By JAMES WALLACE WALKER.

The assumption that all chemical reaction takes place between pre-existing ions is unsatisfactory in that it is incapable of experimental demonstration. In many reactions, the formation of intermediate compounds points to the conclusion that such changes take place in several stages. Some of these compounds can only exist in virtue of the higher valencies possessed by their constituent atoms. Metathetic reactions between the alkyl halides, which take place with great readiness in presence of aluminium chloride, are described and shown to be due to the formation of such compounds; they are accompanied by the production of ionised solutions, but in an analogous case, where the solution is also ionised, the corresponding reaction is excessively slow. Several series of observations point to the conclusion that ionisation is the result of

chemical combination due to potential valency, and that reaction is not dependent in these cases on antecedent ionisation.

The ethers and the alkyl halides are shown to become quite good ionising media when employed in certain reactions in which they are themselves involved, although from their very low dielectric power they would not be expected to have this property. The variation of the molecular conductivity of some of these solutions with varying concentration shows very pronounced maxima and minima, which point to the formation of compounds with the solvent. These maxima and minima correspond in some instances with pronounced colour changes in the solutions. The conclusion is that, in general, combination through the operation of higher valencies precedes ionisation or any other manifestation of chemical change.

*98. "Ionisation and Chemical Combination in the Liquefied Halogen Hydrides and Hydrogen Sulphide." By JAMES WALLACE WALKER, DOUGLAS MCINTOSH, and EBENEZER HENRY ARCHIBALD.

A large number of organic substances are shown to yield solutions which are good conductors of an electric current when dissolved in the liquefied halogen hydrides. Nearly all of those containing oxygen form conducting solutions in one or other of these media. In most of these instances, the ionisation can only take place after combination with the solvent. The importance of the existence of such compounds in depicting the mechanism of some of the fundamental reactions of organic chemistry is pointed out in the preceding communication. Hydrogen sulphide, although an exceedingly good solvent for nearly all classes of substances, yields only a few solutions which conduct at all and very few that conduct well. Almost all of these are, however, cases in which chemical combination between solvent and solute may be assumed.

*99. "Some Compounds of Aluminium Chloride with Organic Substances containing Oxygen." By JAMES WALLACE WALKER and ARTHUR SPENCER.

Compounds of aluminium chloride with ether, anisole, ethyl benzoate, methyl mandelate, ethyl oxalate, ethyl malonate, acetic acid, *o*-nitrotoluene, and *m*-dinitrobenzene have been prepared in order to determine whether there is a proportionality between the number of atoms of oxygen and the number of molecules of aluminium chloride which enter into combination.

In determining the depression of freezing-point of aluminium chloride in *o*-nitrotoluene solution, it was found that this solvent has two crystalline forms, one melting at -10° and the other at -4.25° . The molecular weight of the salt apparently increases with increasing volume.

*100. "The Constituents of *Chaulmoogra* Seeds." By FREDERICK BELDING POWER and FRANK HOWORTH GORNALL.

The seeds which afford the chaulmoogra oil of commerce are derived from *Taraktogenos Kurzii* (King), a native of Burmah, and not, as has until quite recently been assumed, from *Gynocardia odorata* (R.Br.). The oil has previously been examined by Moss ("Year-book of Pharmacy," 1879, 523-533), Petit (*Journ. Pharm. Chem.*, 1892, xxvi., 445), and more recently by Schindelmeyer (*Ber. Deutsch. Pharm. Ges.*, 1904, xiv., 164), but their results differ in many respects from those obtained by the present authors, which are as follows:—

The seeds of *Taraktogenos Kurzii* (King) contain a hydrolytic enzyme, and also an unstable cyanogen compound, which reacts with the enzyme when the seeds are crushed, giving rise to hydrogen cyanide. Numerous attempts were made to isolate this compound, but without success. Further experiments will be made in this direction.

On expression, the seeds yielded 30.9 per cent of a fatty oil, which had the following constants:—M. p. $22-23^\circ$; sp. gr. 0.951 at 25° and 0.940 at 45° ; $[\alpha]_D^{25} +52^\circ$; acid value 23.9 ; saponification value 213 ; iodine value 103.2 .

On hydrolysis, the fatty oil yielded glycerol, a very small amount of phytosterol, $C_{26}H_{43}OH$ (m. p. 132°), and a mixture of fatty acids (m. p. $44-45^{\circ}$; $[a]_D +52.6^{\circ}$ in chloroform; acid value 215; iodine value 103.2), which consisted chiefly of several homologous acids belonging to a series $C_nH_{2n-4}O_2$ containing a closed ring and one ethylenic linking, no member of which has hitherto been isolated from a fatty oil. The highest of these homologues present, which was isolated in a pure condition, separates from most of the usual organic solvents in glistening leaflets (m. p. 68° ; b. p. $247-248$ 20 m.m., $[a]_D +56$), has the formula $C_{18}H_{32}O_2$, and is designated *chaulmoogric acid*. It combines with only two atomic proportions of bromine or iodine. Palmitic acid also was identified, and there is reason for assuming the presence of a near homologue or homologues of chaulmoogric acid, but belonging to the series having the general formula $C_nH_{2n-4}O_2$ with two ethylenic linkings. Undecylic acid and hydroxyacids were proved to be absent, and an individual acid corresponding with hypogaeic acid could not be isolated. The "gynocardic acid" of all previous investigators is believed to be a mixture of several substances.

The "press-cake" yielded, besides formic and acetic acids and a very small amount of volatile esters having the characteristic odour of the seeds, an appreciable amount of a neutral oily substance, $C_{18}H_{32}O_2$, (b. p. $214-215^{\circ}/18$ m.m., sp. gr. 0.9066 at $16/16^{\circ}$, $[a]_D +42.4^{\circ}$), which is isomeric with chaulmoogric acid; this substance is being further investigated, as are also the seeds of *Gynocardia odorata* (R.Br.).

*101. "The Constitution of Chaulmoogric Acid." Part I. By FREDERICK BELDING POWER and FRANK HOWORTH GORNALL.

With the object of ultimately determining the constitution of *chaulmoogric acid*, $C_{18}H_{32}O_2$ (see preceding abstract), a number of its derivatives have been prepared and studied.

Methyl chaulmoograte, $C_{17}H_{31}CO_2Me$ (m. p. 22° , b. p. 227° corr./20 m.m., sp. gr. 0.9119 at $25^{\circ}/25^{\circ}$, $[a]_D 15^{\circ}+50^{\circ}$, in chloroform), was prepared by the interaction of the acid, methyl alcohol, and hydrogen chloride. *Ethyl chaulmoograte*, $C_{17}H_{31}CO_2Et$, a colourless oil (b. p. 230° corr./20 m.m., sp. gr. 0.9079 at $15^{\circ}/16^{\circ}$, $[a]_D 20^{\circ}+50.7^{\circ}$), was prepared in like manner. *Chaulmoogramide*, $C_{17}H_{31}CONH_2$ (m. p. 106° , $[a]_D 27^{\circ}+57.3^{\circ}$ in chloroform), was obtained according to Aschan's method (Ber., 1898, xxxi., 2344). *Bromodihydrochaulmoogric acid*, $C_{17}H_{32}BrCO_2H$ (m. p. $36-38^{\circ}$; optically inactive), is formed when chaulmoogric acid is treated with hydrogen bromide in glacial acetic acid.

Ethyl chaulmoograte absorbs two atomic proportions of bromine in the cold, forming *ethyl dibromodihydrochaulmoograte*, $C_{17}H_{31}Br_2CO_2Et$, which is an oil.

When chaulmoogric acid is treated with sodium in boiling amyl alcohol, the ethylenic linking is not resolved, but there were obtained, after fractional distillation of the product, *chaulmoogryl alcohol*, $C_{18}H_{33}OH$ (m. p. 36° , $[a]_D +58.4^{\circ}$) and *chaulmoogryl chaulmoograte*, $C_{17}H_{31}CO_2C_{18}H_{33}$ (m. p. 42°), together with unchanged chaulmoogric acid.

The saturated acid, *dihydrochaulmoogric acid*, $C_{17}H_{33}CO_2H$ (m. p. $71-72^{\circ}$, b. p. $248^{\circ}/20$ m.m.; optically inactive), is formed, however, on reducing bromodihydrochaulmoogric acid with zinc dust and alcohol, or chaulmoogric acid with hydriodic acid and phosphorus. By the latter process, a hydrocarbon, *chaulmoogrene*, $C_{18}H_{34}$ (b. p. $193-194^{\circ}/20$ m.m.) is also formed. *Methyl dihydrochaulmoograte*, $C_{17}H_{33}CO_2Me$ (m. p. $26-27^{\circ}$, b. p. $222-223^{\circ}/20$ m.m.), was prepared from the corresponding acid.

Chaulmoogric acid is not attacked by fused caustic alkalis even at 300° .

When chaulmoogric acid was oxidised with cold permanganate (1 atom oxygen), *dihydroxydihydrochaulmoogric acid*, $C_{17}H_{31}(OH)_2CO_2H$ (m. p. 102°), was produced, but when the amount of permanganate was equivalent to 4-5 atomic proportions of oxygen, formic acid and two dibasic

acids were obtained, the latter having the formula $C_{15}H_{28}(CO_2H)_2$ and $C_{15}H_{28}O(CO_2H)$ (m. p. 128°). The *ethyl esters* of these acids were described.

The molecular magnetic rotation of ethyl chaulmoograte very closely approximates to the calculated value for an unsaturated ester of the formula $C_{20}H_{32}O_2$, having a closed ring and one ethylenic linking, the latter being contained in an allyl group. This conclusion, based on the magnetic rotation, is in harmony with the results obtained by the oxidation of the acid.

The further investigation of chaulmoogric acid is proceeding.

*102. "Gynocardin, a New Cyanogenetic Glucoside." (Preliminary Note). By FREDERICK BELDING POWER and FRANK HOWORTH GORNALL.

In the course of an examination of the seeds of *Gynocardia odorata* (R.Br.), it was observed that when these were bruised and brought into water a strong odour of hydrogen cyanide is developed. This is due to the presence of a cyanogenetic glucoside, which the authors have isolated in a crystalline state, and designate *gynocardin*. It is very soluble in water, less freely in alcohol, and crystallises from these solvents in colourless needles which melt at $161-162^{\circ}$ with slight decomposition, and have $[a]_D 19^{\circ}+37.1^{\circ}$; it gave on analysis the following percentages:—C=48.0; H=5.8; N=4.3. Its constitution is being determined.

103. "isoNitrosocamphor." By MARTIN ONSLOW FORSTER.

An unstable isnitrosocamphor (m. p. 114°), produced by the action of sodium and amyl nitrite on camphor, is converted into the yellow benzoyl derivative (m. p. $105-106^{\circ}$) on treatment with benzoyl chloride in pyridine, whilst the colourless benzoyl derivative (m. p. 136°) is produced in a similar manner from the stable isnitrosocamphor (m. p. 152°).

Potassium ferrocyanide oxidises both forms to an unstable *peroxide*, $C_{20}H_{28}O_4N_2$, which is insoluble in alkalis, and, the more fusible isnitrosocamphor being attacked first, the isomerism can be freed from it by using insufficient oxidising agent.

The *O-methyl ether of isnitrosocamphor*, $C_{17}H_{17}O_2N$, obtained by the action of methyl iodide in presence of silver oxide, crystallises in rectangular plates, melts at 107° , and has $[a]_D +197.7^{\circ}$. Reduction converts it into aminocamphor, hydrolysis resolves it into α -camphornitrilic acid, and hydroxylamine gives rise to the *oxime*, $C_{17}H_{18}O_2N_2$, which melts at 188° and has $[a]_D -95.3^{\circ}$.

The *N-methyl ether of isnitrosocamphor*, $C_{17}H_{17}O_2N$, produced in association with the isomerism when methyl iodide acts on isnitrosocamphor dissolved in alcoholic potash, is a pale yellow oil which decomposes on distillation and has $[a]_D +297.8^{\circ}$. Dilute acids and alkalis hydrolyse the substance to camphorquinone and β -methyl-hydroxylamine, reduction with zinc dust and acetic acid converting it into methylaminocamphor; hydroxylamine gives rise to isnitrosocamphor and the β -dioxime of camphorquinone, whilst phenylhydrazine transforms it into camphorquinonephenylhydrazine.

The decomposition of the colourless benzoyl derivative of isnitrosocamphor on exposure to light yields the anhydrides of benzoic and α -camphornitrilic acids, the yellow isomeride giving rise to the same products. Determinations of molecular weight reveal no difference between the isomeric-benzoyl derivatives.

The following derivatives of the camphorquinone dioximes have been examined:—The *acetyl* α -dioxime (m. p. $148-149^{\circ}$), the *dibenzoyl* α -dioxime (m. p. 153°), the *diacetyl* β -dioxime (m. p. 119°), the *dibenzoyl* β -dioxime (m. p. 189°), the *benzoyl* γ -dioxime (m. p. 172°), and the *dibenzoyl* γ -dioxime (m. p. 150°).

104. "The Basic Properties of Oxygen. Additive Compounds of the Halogen Hydrides and Organic Compounds, and the Higher Valencies of Oxygen. Asymmetric Oxy-

gen." By EBENEZER HENRY ARCHIBALD and DOUGLAS MCINTOSH.

An account was given of the preparation and properties of a number of compounds in which oxygen assumes a valency higher than 2.

The following compounds have been prepared and analysed:—

Acetone yields the hydriodide, $(\text{CH}_3)_2\text{CO}\cdot\text{HI}$; the hydrobromide, $(\text{CH}_3)_2\text{CO}\cdot\text{HBr}$; and the hydrochloride, $[(\text{CH}_3)_2\text{CO}]_2\cdot\text{HCl}$.

Ether gives rise to the compounds $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HI}$, $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HBr}$, and $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HCl}$.

Ethyl alcohol furnishes the following series:—
 $\text{C}_2\text{H}_5\cdot\text{OH}\cdot 2\text{HI}$, $\text{C}_2\text{H}_5\cdot\text{OH}\cdot 2\text{HBr}$, and $\text{C}_2\text{H}_5\cdot\text{OH}\cdot 5\text{HCl}$.

These products are white compounds, crystallising readily from their solutions in the liquefied halogen hydrides and melting at temperatures varying between -120° and -9° ; they are prepared by mixing together the organic compound previously cooled to -80° with the appropriate halogen hydride in the liquid state, considerable quantities of heat being generated by the reaction.

A compound of anisole and hydrogen bromide has been prepared, which is probably phenylmethyloxonium bromide having the constitution $\text{CH}_3 > \text{O} < \text{H}$
 $\text{C}_6\text{H}_5 \quad \text{Br}$ and therefore containing an asymmetric oxygen atom. This and similar compounds are at present under investigation.

105. "The Fermentation of the Indigo Plant." By CYRIL BERGTHEIL.

The fermentation of the indigo plant has been ascribed to a bacterium and also to enzymes, but has hitherto never been satisfactorily investigated. The author shows that, although there are many bacteria capable of producing the fermentation, it is in the main due to a specific enzyme occurring in the plant cells. A very active solution of this enzyme has been obtained, and the course of the fermentation produced by adding this to an extract of the indigo plant made in boiling water has been studied. It is found that the fermentation proceeds in a similar manner to that observed by Adrian Brown for invertase (*Trans.*, 1902, lxxxi., 273) and by Horace Brown and Glendinning for diastase (*Trans.*, 1902, lxxxi., 388), namely, that equal quantities of substance are transformed in equal intervals of time in the early stages, but not in the later ones. The point at which the course of the change can no longer be represented by a straight line is when 17 to 20 per cent of the total action has taken place. The curve representing the reaction ceases to be linear at about the same point when the time factor is kept constant, but the quantity of acting enzyme varied.

The optimum temperature for the action is almost exactly 50° , and the temperature at which the enzyme is destroyed is 71° . The rate of action is decreased by the presence of both acids and alkalis. Sodium acetate up to 1 per cent does not affect the rate of action. Various antiseptics all produced inhibition, formalin to the greatest, and boric acid to the least extent. Emulsin can produce the indigo fermentation, but has a very weak action. It is doubtful whether the indigo enzyme can decompose amygdalin. Myrosin cannot ferment an extract of the indigo plant, and the indigo enzyme cannot ferment sinigrin. No evidence of the existence of an oxidase in the indigo plant was obtained.

106. "The Union of Hydrogen and Chlorine. Action of the Silent Discharge on Chlorine." By JOSEPH WILLIAM MELLOR.

By means of a special apparatus, chlorine can be subjected to any desired treatment before admixture with hydrogen without disturbing the equality of the proportions of hydrogen and chlorine in Bunsen and Roscoe's actinometer. The electrolytic gases are first sent through the liquid in the insulation vessel until a state of equilibrium is attained; the gases are then led into the insulation vessel without bubbling through this liquid at all.

If the chlorine gas is led through a glass "ozone apparatus" before admixture with hydrogen, the period of induction is curtailed, as indicated in the third column of the accompanying table. The numbers in the fourth column were obtained by the same apparatus, but the chlorine was exposed to the light of an acetylene flame before admixture with hydrogen. The numbers in the second column were obtained with chlorine not subjected to any previous treatment.

Time, in minutes.	Ordinary chlorine.	Movement of index with—	
		1. Chlorine and silent discharge.	2. Chlorine and acetylene light.
1	0.1 c.m.	1.8 c.m.	2.5 c.m.
2	0.1 "	4.4 "	4.2 "
3	0.4 "		
4	1.5 "		
5	3.0 "		
6	4.0 "		

(The asterisk denotes that the gases afterwards united at a constant rate).

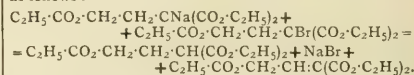
Moist chlorine is more chemically active towards hydrogen when subjected to—(1) A preliminary exposure to light; or to (2) a silent discharge of electricity.

Attempts are being made to isolate the active component.

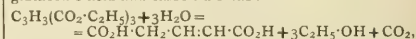
107. "Studies on Ethyl Carboxyglutarate. Part II. Action of Ethyl Bromocarboxyglutarate on Ethyl Sodiocarboxyglutarate. Formation of Ethyl Carboxyglutamate." By OSWALD SILBERRAD and THOMAS HILL EASTERFIELD.

It was shown by the authors in the former part of the present work (*Proc.*, xx., 114) that ethyl sodiocarboxyglutarate is converted into haloal derivatives of ethyl carboxyglutarate by the action of halogens, no ethyl carboxyglutarate being formed. For this reason, the reaction between ethyl bromocarboxyglutarate and ethyl sodiocarboxyglutarate has been examined.

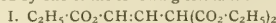
On bringing together the haloal and sodium derivatives of ethyl carboxyglutarate, they react and give rise to a mixture of the original ethyl carboxyglutarate and a new unsaturated ester, $\text{C}_{12}\text{H}_{18}\text{O}_6$. The reaction, which appears to be unlike anything hitherto observed, may be represented as follows:—



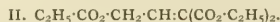
This unsaturated ester is thus to be regarded as ethyl α -carboxy- $\Delta^{\alpha\beta}$ -glutamate. On saponification, it yields a new carboxyglutamic acid, which readily breaks up into glutamic acid and carbon dioxide:—



from which it will be seen that its constitution must be represented by one of the following formulae:—



or—



The latter of these formulae must be the correct one, since the former represents ethyl isocitronate, from which the new isomeride differs in containing no active hydrogen and hence forming no sodium derivative.

108. "The Vapour Pressures of Liquid Mixtures of Restricted Mutual Solubility." (Preliminary Notice). By ARTHUR MARSHALL.

Although this subject has been somewhat fully treated from the theoretical side by Margules, Ostwald, Duhem, and others, yet with the exception of some somewhat rough measurements published by Konowaloff in 1881 and by Schrienemakers in 1890, no actual experiments have been made to test their conclusions. Experiments on mixture of water with ether, methyl acetate, and more especially

ethyl methyl ketone, have shown that in each case the curve for the total vapour pressure has much the same shape, but that this form is slightly different to those predicted by the foregoing authors.

When one of these comparatively volatile organic liquids is added gradually to water, the vapour pressure rises rapidly until the water becomes saturated. A second liquid phase then ensues and the curve becomes a horizontal straight line in accordance with the phase rule. When sufficient of the liquid has been added to dissolve the water completely, the curve again rises until it reaches a maximum, after which it falls again, until at 100 per cent it coincides with the vapour pressure of the pure substance. It is in this portion of the experimental curve that the variation from the predicted forms is noticeable.

In consequence of this peculiarity, the liquid mixture, unless containing a very large proportion of one or other of its constituents, will yield a distillate having a composition approximating closely to that which gives the maximum point. For example, with mixtures of methyl ethyl ketone and water, if the original liquid contains between 10 and 90 per cent of the ketone, the distillate will contain about 88·6 per cent of this compound.

109. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part V. The Optical Activity of Certain Tartrates in Aqueous Solution." By THOMAS SELLWICK PATERSON.

The rotations of sodium tartrate, potassium tartrate, potassium methyl tartrate, potassium ethyl tartrate, potassium *n*-propyl tartrate, methyl tartrate, ethyl tartrate, and *n*-propyl tartrate have been examined in aqueous solution at several concentrations and at temperatures between 10° and 100°.

In very dilute solution, sodium and potassium tartrates behave alike both as regards rotation value and influence of temperature-change, the rotation increasing as the temperature is raised.

It was shown that the rotations of the homogeneous compounds, could they exist in a superfused condition, would diminish on heating from 0° to 100°.

Of the three potassium alkyl tartrates, the *n*-propyl ester had the highest, and the methyl ester the least rotation, both in dilute solution and in the homogeneous state. Dilute solutions of these compounds all showed distinct temperatures of maximum rotation.

The rotations of the three alkyl tartrates were all raised by solution in water, and in dilute solution the rotations diminished rapidly on heating, this behaviour being just the opposite of that shown by the homogeneous esters.

The rotations in very dilute solution of the compounds examined were compared with each other and with that of the tartaryl ion.

The relationships existing among the experimental data were discussed with reference to the variations produced by solution and by change of temperature, and some suggestions, based on these observations, were advanced with respect to the temperatures at which the comparisons of rotation values may legitimately be instituted.

110. "The Nitration Products of the Isomeric Dichlorobenzenes." By PERCIVAL HARTLEY and JULIUS BEREND COHEN.

The progressive nitration of the dichlorotoluenes has been investigated by Cohen and Dakin (*Trans.*, 1902, lxxxi., 1344), and the results show that the two nitro-groups in the dinitro-derivatives of the six dichlorotoluenes follow strictly the meta-law of substitution.

Since the publication of the above, three papers describing the nitration products of *o*-, *m*-, and *p*-dichlorobenzenes have appeared (Morgan, *Trans.*, 1902, lxxxi., 1378; Blankens and Tervoght, *Rec. Trav. Chim.*, 1902, xxi., 286; and Blankens, *Ibid.*, 419).

From this it would appear that the principal products of nitration are an ortho-dinitro-compound in the case of *o*-dichlorobenzene, a meta-dinitro-compound in the case of *m*-dichlorobenzene, and a para-dinitro-compound in the

case of *p*-dichlorobenzene. The authors have repeated the work in order to ascertain quantitatively how far the divergence from the meta-law holds good.

They have been able to confirm the results of nitration of the *o*- and *m*-dichlorobenzenes, but not of the para-compound. The first gives with great difficulty an ortho-dinitro-compound, the second much more easily a meta-dinitro-compound, but *p*-dichlorobenzene gives about six times as much of the meta-dinitro-compound as of its para-isomeride. The only important exception to the meta-law is therefore afforded by *o*-dichlorobenzene.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE: All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxcviii., No. 20, May 16, 1904.

Electrolysis of Calcium Chloride.—Henri Moissan.—In answer to M. Bullier's claim of priority of the electrolysis of calcium chloride, the author explains that his experiments differ from those of M. Bullier—(1) Because he has a liquid bath easily electrolysable; (2) because, even in the presence of carbon, more calcium than carbide is produced. In the author's first experiments he electrolyses a mixture of chloride and fluoride of calcium, and M. Bullier does not appear to have used such a bath at all.

The Density of Aqueous Saline Solutions considered as an Additive Property of the Ions. Existence of certain Hydrated Ions.—P. Vaillant.—Unsuitable for abstraction.

New Method of Exact Determination of the Molecular Weight of Permanent Gases. Atomic Weight of Hydrogen, Carbon, and Nitrogen.—Ph. A. Guye.—During numerical investigations on the fluid equation, the author establishes the fact that Van der Waals's equation leads to the relation $V_m(1 + a)(1 - b) = R$; where V_m is the volume of a gram-molecule at 0° and 760 m.m., a and b the two constants of the fluid equation, and R the constant of perfect gases (22410·4). When applying this relation to the finding of the molecular weight of the so-called permanent gases (whose critical-point is below zero) the following modification is necessary: $-V_m(1 + a)(1 - b) = R - mT_c$; m having the value 0·08473, the correction for mT_c always being very small. To determine the molecular weight deduced from gaseous densities the expression can be written $M = \frac{L}{1000} \frac{R + mT_c}{(1 + a)(1 - b)}$.

Preparation and Properties of Hypophosphorous Acid.—C. Marie.—The author describes a method of preparing hypophosphorous acid by a modification of Thomsen's method. When a large quantity is prepared, it is purified by fractional crystallisation, and on cold days the crystals can be filtered at the pump and left to dry for several days over phosphoric anhydride. Careful experiments show the fusion-point of this substance to be 26·5°. Hypophosphorous acid is decomposed by heat in the following manner: $-2PO_2H_3 = PO_4H_3 + PH_3$.

A Crystalline Chromous Tartrate.—G. Baugé.—The author finds that tartaric acid forms with chromium protoxide a crystalline anhydrous compound having a blue colour, and which is proved by analysis to have the formula $C_4H_4CrO_6$.

Triphenylmethane Colouring Matters.—Charles Lauth.—The author applies the reaction of replacing the hydrogen of the NH_2 group in the aromatic amines by various substitutes to those leuco-bases of triphenylmethane which, after hydroxylation, sulphonation, and oxidation, give rise to very rich colouring matters

possessing the rare property of being unaltered by alkalis. Particularly, these substitutions were tried in leuco-derivatives which are obtained by the reduction of the condensation products of the essence of manitrat bitter almonds on dimethyl- or diethylaniline. A series of substitution agents were made to act on these leuco-bases, and the products thus obtained examined from the point of view of the colouring matter which they form. The most interesting results are those given by the derivatives of acetyl chloride or acetic anhydride and the chloride of benzenesulphonic acid, $C_6H_5SO_2Cl$. Blue colouring matters are thus obtained analogous to patent blue, and possessing the same qualities of resistance towards alkalis, besides purity of shade. With the non-substituted amine derivative, greens are obtained.

Preparation of $\alpha\beta$ -Diketonic Ethers.—L. Bouveault and A. Wahl.—The authors examine the constitution of certain phenylhydrazones and their relationship with the isomeric compounds resulting from the action of diazobenzene chloride on acetylacetic ether. They also propose to generalise this reaction, in order to arrive at the preparation of the $\alpha\beta$ -diketonic ethers, $R-CO-CO-COOC_2H_5$.

Action of PCl_3 on certain Cyclic Primary Amines at Boiling-point. Reduction of PCl_3 with Formation of Phosphorus.—P. Lemoult.—The author finds that when PCl_3 reacts on the cyclic amines, RNH_2 , at their boiling-point, there are formed, besides the orange compound described in a former paper, the same products which PCl_3 gives without a gaseous evolution, but with production of white phosphorus.

New Polymers of Formaldehyde.—A. Seyewetz and M. Gibello.—Up to the present time four polymers of formaldehyde have been described. The author prepares other polymers having absolutely different properties, of which a list is given.

Action of Paraformaldehyde on the Sesquiterpenes. P. Genvesse.—MM. Ladenburg and Krievitz examined the action of paraformaldehyde on certain terpenes in sealed tubes, and they obtained addition products with alcoholic function. The author finds that the sesquiterpenes behave in the same manner with trioxymethylene, but the action is not quite so easy and the yields smaller. His experiments were chiefly with a view to obtaining perfumes, and he shows that caryophyllene, clovene, and cadinene will combine molecule for molecule with formic aldehyde.

Bulletin de la Société Chimique de Paris.

Séries 3, Vol. xxix., Nos. 18—19.

Normal Existence of Arsenic in all the Organs of the Animal Economy.—Armand Gautier.—The author's experiments show that arsenic exists normally in certain tissues, animal and vegetable, and that it is absent, or in unappreciable quantities, in many others. He is not yet satisfied—as some writers are—that this metalloïd is present in all living cells.

Electrolytic Separations. 1. Manganese and Iron. 2. Aluminium and Iron, or Nickel; Zinc and Iron.—MM. Holland and Bertiaux.—Already noticed.

Estimation of the Persulphates.—C. Marie and L. J. Brunel.—Already inserted in full.

Ratio between the Solubility of Lime in the presence of Alkalis, and the Caustification of the Alkaline Carbonates.—Alex. d'Anselme.—The author finds that the solubility of lime in water diminishes sensibly when the temperature is increased; it also diminishes when the temperature is constant if the proportion of caustic soda is augmented. With a constant quantity of caustic soda, the solubility diminishes when the temperature rises.

Examples of the Complexity of the Catalytic Action of Metals: Vivifying and Paralysing Influences.—M. Trillat.—Already noticed.

New Method for the Attack of Galenas and Chalcopyrites.—C. Boucher.—Already inserted in full.

Manner of Division of Mixed Organo-magnesian Compounds. Action of Oxide of Ethylene.—V. Grignard.—Already noticed.

Action of Chloride of Ethoxylal on the Organo-magnesian Compounds.—V. Grignard.—Already noticed.

Primary Phenylethyl Alcohol.—V. Grignard.—This alcohol was obtained by the action of commercial polyoxymethylene on benzylchloride of magnesium, according to the method already discovered by the author in collaboration with M. Tissier. The primary phenylethyl alcohol thus obtained has a fairly agreeable aromatic odour; it crystallises, by cooling under a current of water, in long needles fusible at 33° ; its density taken at surfusion at 15.2° is 1.0389.

Method for the Preparation of Diethylacetacetate of Methyl.—V. Grignard.—Dissolve 11.5 grms. of sodium in 70 grms. of methanol, add half a molecule of acetic ether, half a molecule of iodide of ethyl, and heat (with a reflux condenser) for two hours. When the alkalinity has almost completely disappeared, distil a portion of the methylic alcohol on the water-bath, treat the residue with water, and then in the usual manner. The product obtained separates into two portions by fractional distillation. The most important boils at $187-190^\circ$ under 750 m.m.; this is the ethylacetacetate of methyl. The other is the corresponding ethylic ether. These were treated separately with iodide of ethyl and methylate of sodium in methylic solution. In both cases nothing but diethylacetacetate of methyl was obtained.

Preparation of Nitric Ethers.—L. Bouveault and A. Wahl.—Already noticed.

Preparation of the Nitrous Ethers of Alcohols.—L. Bouveault and A. Wahl.—Already noticed.

Isonitrosomalonic Ethers.—L. Bouveault and A. Wahl.—Already noticed.

Action of Chloracetimide on some Aromatic Amines.—A. L. Lumière and F. Perrin.—The authors have obtained a series of nine new compounds by reacting with chloracetimide on an amine of the type $R-NH_2$ or $R'>NH$, a molecule of hydrochloric acid is eliminated, and the radical $-CH_2-CO-NH_2$ becomes joined to the group NH of the amine.

Action of Phenylhydrazine on the Alcoholic Bromides and Iodides.—J. Allain-le Canu.—Already noticed.

Cyclohexane and its Chlorised Derivatives.—P. Sabatier and A. Mailhe.—The physical properties of the cyclohexane C_6H_{12} are identical with those of the carbide prepared synthetically from pimelic acid by Żelinski. The existence of the aromatic nucleus in this carbide was proved by the action of bromine, which changes it into tetrabromobenzene. It is also shown by the reactions of the chlorised derivatives, which are fully described in this paper.

Separation of the Principles Decomposing Peroxide of Hydrogen contained in the Hæmatin.—J. Ville and J. Moitessier.—The authors have obtained a ferment from blood, and show that it is the fixation of this ferment on the fibrin that is the essential, if not the exclusive, cause of the decomposing action of this proteic principle on peroxide of hydrogen.

Influence of the Nature of the Surroundings on the Formation and Evolution of the Odorous Compounds in Plants.—E. Charabot and A. Hebert.—A long paper, not suitable for abstraction.

A New Gas Burner.—L. Quennessen.—Already noticed.

MISCELLANEOUS.

The Absorption Spectra of Solutions of Salts of Didymium containing Phosphoric Acid, and on Orthophosphate of Didymium.—A. Waegner.—The addition of PO_4H_3 in excess to a solution of chloride of didymium gives a fairly stable limpid solution; its absorption spectrum is not the same as that of the primitive salt. The bands are decidedly displaced, and especially those near the D line, which are replaced by a large number of narrower bands (see plate in the original). On the addition of water, or by increasing the temperature, the solution gives a precipitate of phosphate of didymium; the best way is to pass a strong current of steam through the solution. A pinkish-white amorphous precipitate is formed, becoming quite white on calcination, attackable only by concentrated acids after calcination. This salt is $\text{PO}_4\text{Di}_2\text{H}_2\text{O}$ (at 100°). It gives a very characteristic emission spectrum. The anhydrous PO_4Di , treated with concentrated SO_4H_2 , becomes heated, and is partially dissolved; if we evaporate strongly to drive off the excess of SO_4H_2 , there remains a residue of sulphate and metaphosphate of didymium.—*Berichte*, vol. xxxvi., p. 3055.

Examination of the Methods for the Estimation of Antimony.—L. A. Youtz.—The boiling-points of the chlorides of antimony, arsenic, and tin are very different (230° , 134° , and 114°). On the other hand, they volatilise from their hydrochloric acid solutions at totally different temperatures. Tin (as SnCl_4) keeps nearest to its boiling-point, 114° , but antimony and arsenic commence to volatilise respectively at 108° and 75 – 80° . Whether the antimony is in solution in the antimonious or the antimonim form, its volatility is the same. As the chloride, SbCl_3 , prepared from Cl and Sb, is much more volatile than the trichloride, we are inclined to admit that the latter is hydrolysed in solution in $\text{HCl} + \text{SbO}_4\text{H}_3$. It should be the same in solutions in which the antimony has been dissolved by a mixture of NO_3H and ClO_3K . Further, we cannot attribute this slight volatility to the formation of double salts, for the same results are observed by oxidising with a mixture of $\text{NO}_3\text{H} + \text{HCl}$. This facility for hydrolysing is also observed with all the elements of the group, and becomes fainter from P to Bi.—*Zeit. Anorg. Chem.*, vol. xxxv., p. 55.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC, As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, &c.

E. GEORGE & SONS,
BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.,

ARE OPEN TO PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1898 to 1899, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased. Current Catalogue of General Literature sent on application.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.

LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO., 21, Mincing Lane, London, E.C., who hold stock ready for delivery.

A Selection from

MACMILLAN & CO.'S BOOKS FOR STUDENTS OF CHEMISTRY.

FRACTIONAL DISTILLATION. By SYDNEY YOUNG, D.Sc., F.R.S., Professor of Chemistry in University College, Bristol. With 72 Illustrations. Crown 8vo, 8s. 6d.

AN INTRODUCTION to the STUDY of CHEMISTRY. By Prof. W. H. PERKIN, Jr., Ph.D., F.R.S., and BEVAN LEAN, D.Sc., B.A. (Lond.). Globe 8vo, 2s. 6d.

A PRIMER of CHEMISTRY. By Sir HENRY E. ROSCOE, F.R.S. Illustrated. With Questions. Pott 8vo, 1s.

INORGANIC CHEMISTRY for BEGINNERS. By Sir HENRY E. ROSCOE, F.R.S. Assisted by JOSEPH LUNT, B.Sc. Globe 8vo, 2s. 6d.

LESSONS in ELEMENTARY CHEMISTRY, INORGANIC and ORGANIC. By Sir H. E. ROSCOE, F.R.S. Sixth Edition, thoroughly revised. Fcap. 8vo, 4s. 6d.

INORGANIC CHEMISTRY FOR ADVANCED STUDENTS. By Sir H. E. ROSCOE, F.R.S., and Dr. A. HARDEN. Globe 8vo, 4s. 6d.

A TREATISE on CHEMISTRY. By Sir H. E. ROSCOE, F.R.S., and the late C. SCHORLEMMER, F.R.S. Completely revised by Sir H. E. ROSCOE, assisted by Drs. H. G. COLMAN and A. HARDEN. 8vo. Vol. I. The Non-Metallic Elements. 21s. Vol. II. The Metals. 31s. 6d. Vol. III. The Chemistry of the Hydrocarbons and their Derivatives, or Organic Chemistry. Parts II., IV., and VI., 21s. each. Part III., 18s.

INTRODUCTORY CHEMISTRY FOR INTERMEDIATE SCHOOLS. By L. M. JONES, B.Sc. Globe 8vo, 2s.

CHEMISTRY FOR ORGANISED SCHOOLS OF SCIENCE. By S. PARRISH, B.Sc. With Introduction by Dr. FORSYTH. Globe 8vo, 2s. 6d.

PRACTICAL INORGANIC CHEMISTRY. By G. S. TURPIN, D.Sc. Globe 8vo, 2s. 6d.

LESSONS in ORGANIC CHEMISTRY. By G. S. TURPIN, D.Sc. 2s. 6d.

A TEXT-BOOK of INORGANIC CHEMISTRY. By Prof. IRA REMSEN. 8vo, 16s.

INORGANIC CHEMISTRY. By Prof. I. REMSEN. Crown 8vo, 6s. 6d.

ORGANIC CHEMISTRY. By Prof. I. REMSEN. Crown 8vo, 6s. 6d.

The ELEMENTS of CHEMISTRY. By Prof. I. REMSEN. 11th Impression. Fcap. 8vo, 2s. 6d.

COLLEGE TEXT-BOOK of CHEMISTRY. By Prof. I. REMSEN. Extra Crown 8vo, 8s. 6d. net.

A JUNIOR COURSE of PRACTICAL CHEMISTRY. By FRANCIS JONES, F.R.S.E., F.C.S. With a Preface by Sir H. E. Roscoe, F.R.S. Eighth Edition. Globe 8vo, 2s. 6d. Questions, 3s.

PRINCIPLES of INORGANIC CHEMISTRY. By HARRY C. JONES, Associate Professor of Physical Chemistry in the Johns Hopkins University. 8vo. 17s. net.

ELEMENTS of PHYSICAL CHEMISTRY. By Prof. HARRY C. JONES. 8vo. 17s. net.

ELEMENTS of INORGANIC CHEMISTRY. By Prof. HARRY C. JONES. Cr. 8vo. 6s. 6d.

MACMILLAN & CO., Ltd., LONDON.

ST. MARY'S HOSPITAL MEDICAL SCHOOL, PADDINGTON, W. LECTURER ON CHEMISTRY.

Applications for the above Post are invited on or before WEDNESDAY JULY 6, 1904.
Salary £150 per annum (with some extra fees).
Particulars as to duties on application.

H. A. CALEY, M.D., F.R.C.P., Dean.

LONDON COUNTY ASYLUM, HANWELL, W.

The Sub-Committee for the control and management of the above-named Asylum are prepared to receive offers for the Purchase of TAR and AMMONIACAL LIQUOR for the twelve months ending JUNE 30, 1905.

Terms, cash on removal. Forms of Tender, with estimated quantities for sale, may be obtained on application to the Resident Engineer at the Asylum.

Tenders must be sent in sealed covers, endorsed "Tender for Tar and Liquor, Hanwell Asylum," to the undersigned by or before 10 o'clock a.m. on SATURDAY, JULY 2, 1904.

The Sub-Committee do not bind themselves to accept the highest or any Tender.

R. W. PARTRIDGE,
Clerk of the Asylums Committee.

London Asylums Committee Office,
6, Waterloo Place, S.W.,
June 15, 1904.

BOROUGH OF SWANSEA TECHNICAL COLLEGE.

LECTURER IN METALLURGY.

Applications are invited for the above Lectureship. Salary £200 per annum, rising by annual increments of £10 to £250.

The Lecturer will be expected to enter upon his duties in September.

Applications, with one set of copies of testimonials, should reach the undersigned not later than THURSDAY, JUNE 30th.

Further particulars can be obtained from the SECRETARY at the College.

J. TREVOR OWEN, M.A., Principal.

UNIVERSITY COLLEGE of WALES, ABERYSTWYTH.

ASSISTANT LECTURER and DEMONSTRATOR IN
CHEMISTRY.

The Council invite applications for the Post of ASSISTANT LECTURER and SENIOR DEMONSTRATOR in CHEMISTRY.

Applications, together with copies of testimonials, should reach the undersigned, from whom further particulars may be obtained, not later than SATURDAY, JULY 9, 1904.

T. MORTIMER GREEN, Registrar.

June, 1904.

UNIVERSITY OF BIRMINGHAM.

The Council invites applications for the following Appointments:-

ASSISTANT LECTURER in MATHEMATICS.

ASSISTANT LECTURER and DEMONSTRATOR in PHYSICS.

ASSISTANT LECTURER and DEMONSTRATOR in CHEMISTRY.

The stipend in each case will be £150 per annum.

The Candidates selected will be required to enter on their duties on October 3rd next.

Further particulars may be obtained from the undersigned, to whom Applications, accompanied by six copies of testimonials, should be sent not later than AUGUST 1st, 1904.

GEO. H. MORLEY, Secretary.

BRYAN CORCORAN LIM.

MILLSTONE BUILDERS.
WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.



Sole Makers of MILBURN'S
Patent Conoidal Stone Grinding Mills.
Especially suitable for certain materials, Wet or Dry
Works and Warehouses: Back Church Lane
Parsell Dept.: Basement of the Corn Exchange
31, MARK LANE, LONDON.

RADIUM ON SALE AND LET ON HIRE.—Write for terms.

The following can be had by return of post.

Pitchblende, direct from Joachimsthal, very radio-active, from 1/- to 30/- per piece.

Itacolomite, or flexible sandstone, 10/- to 25/- per piece (very rare).

Kunzite, 1/- per gramme. Selected, clear, 2/-

Spartelite (see NATURE, 31/3/04, fol. 523), 2/- and upwards.

Chlorophane, 2/- and upwards Barium Platino Cyanide in large Crystals in course of manufacture. (ORDERS BOOKED).

Zinc Sulphide. Phosphorescing a beautiful Green, 2/6 per tube.

" " " Yellow, 2/6 "

Calcium Sulphide " " Violet, 1/- "

Radio-active Residue from which Radium is made; very scarce, 2/- tube.

Polonium Sulphide, in tubes of one gramme, 21/-

" on Bismuth Rod or Disc, ... 25/-

" on Copper " " " 25/-

Radio-active Screens (Willenite), 6d. per sq. inch. Plat. Bar.

" " (Zinc Sulph.), 9d. per sq. inch.

" " " (Zinc Sulph.), 10 x 10 cm. 7/6.

Professional Men, Universities, Schools, &c., allowed special terms

Our newly invented Thorium Inhalers may be had on hire.

ARMBRECHT, NELSON & CO., 71 & 73 DUKE ST., GROSVENOR SQ., LONDON, W.

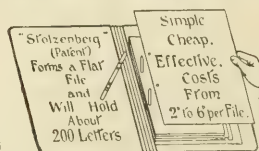
Telephone: GERRARD 492.

N.B.—We have to-day received a consignment of the New Zealand Vegetable Caterpillar; it is from 2 to 3 inches long, with a stem showing fructification growing out of its head. Scientific name of the insect is *Heliphus virescens*; the name of the fungus is *Sphaeria Robertiana*. Specimens may be had from 10/6 to 21/-, according to quality and size.

TERMS CASH WITH ORDER.

Goods may be returned if not approved of, when money will be refunded.

Perfect Order amongst your Scientific Papers, Research Records, &c., IS SECURED BY THE "STOLZENBERG" SYSTEM OF FILING.



The "Unit" of the System is a simple Flat File, made in six distinct colours, for classifying under Subjects, &c.

Used by SIR WILLIAM CROOKES, LORD KELVIN, Royal Commission on Tuberculosis, Baden Aniline Works (50,000), and by thousands of private persons as well as Business Concerns.

Satisfaction guaranteed; otherwise goods taken back and money returned.

Sample Set, consisting of 12 best Files, 4to and fcap., with strong nickel-plated Perforator, and Patent Lifter, packed in leather-board box, 10/6 post free.

THE STOLZENBERG PATENT FILE CO.,
50, Bishopsgate St. Without, London, E.C.

THE CHEMICAL NEWS.

VOL. LXXXIX., No. 2326.

THE

SPECTRUM OF THE RADIIUM EMANATION.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.,

and
Prof. J. NORMAN COLLIE, F.R.S.

ATTEMPTS have been made since July, 1903, to see and map the spectrum of the emanation from radium, for at that date the conversion of the emanation into helium was observed by Ramsay and Soddy, and during the first discharge of the induction current through the emanation, it was believed that a peculiar spectrum was noticed; indeed, three lines were persistent, and were mentioned in the communication on the subject in the *Proceedings*.

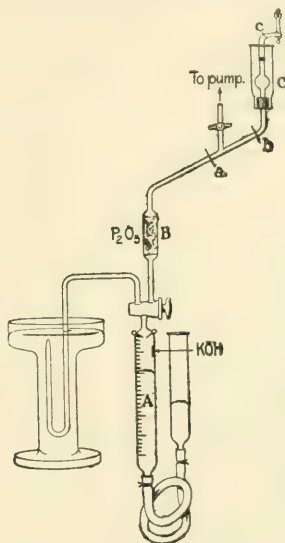
But such attempts have uniformly failed; at the first moment of the discharge, indeed, a brilliant spectrum has twice been observed, which soon became confused and indistinct. It faded before it was possible to map it, and owing to the presence of impurities, generally carbon monoxide, nitrogen, or hydrogen, the special spectrum was obscured. All that could be said was that it appeared to present some brilliantly green lines.

These experiments, however, have not been fruitless; they have led to better knowledge of the precautions which it is necessary to take to eliminate impurities. The arrangement of the apparatus, too, has been simplified, and the manipulation made easier. As it is possible that others may wish to repeat the experiments, and may perhaps have even better success in mapping the spectrum, we think it well to enter into the details of the manipulation somewhat minutely, and to give a woodcut of the apparatus employed.

The stock of radium bromide (about 100 m.grms.) dissolved in about 10 c.c. of water in two small bulbs was attached by sealing to a small Töpler's pump. Between the pump and the bulb there was a stop-cock, greased of course, to ensure freedom from leakage, but in order to prevent the long contact of the emanation with the stop-cock, and its possible contamination with carbon dioxide, the mercury from the pump was caused to flow past the stop-cock by raising the reservoir of the pump and closing the exit tube at its lower end; the mercury slowly leaked past the valve of the pump, passed the tap (which was then shut), and so confined the space above the radium bromide by means of mercury. As radium bromide yields electrolytic gas, containing an excess of hydrogen, the pressure gradually rose; the mercury in contact with this gas remained perfectly bright, and showed no tendency to adhere to the glass; the presence of ozone thus appears to be excluded, but this excess of hydrogen will form the subject of a future communication.

The emanation was allowed to accumulate for fourteen days. The pump was exhausted until no trace of a bubble passed down the capillary exit tube. But as even then a trace of air must have remained in the barrel, the tap leading to the bulbs containing the radium bromide was turned rapidly, so as to admit a trace of the electrolytic gas into the pump and "wash it out." This gas was rejected. The remaining electrolytic gas with the emanation was collected in a tube which had previously been heated to redness, and then twice washed out with pure oxygen. The mercury in the collecting tube was then boiled, and the bubble of gas removed. It was hoped thereby to have eliminated every trace of nitrogen. The gas was then introduced into the gas-burette, shown in the figure, through

the inverted syphon. All the mercury was freshly filtered and pure. The apparatus, too, was freshly constructed and heated to redness to burn out traces of dust. The gas-burette had been washed out with alkali and with nitric acid, and then with a stream of distilled water; it was dried by drawing through it a stream of dust-free air. Some slightly moist caustic potash was melted on to the glass, near the sparking wires; this was intended to absorb any trace of carbon dioxide which might have chanced to be formed during the explosion of the electrolytic gas by the burning of dust. The rubber tube was cemented on to the burette; the burette was washed out twice with oxygen, and by lowering the reservoir several times the upper end was made a torricellian vacuum; it was left thus for some time, so as to ensure the removal of adhering nitrogen from the walls of the tube.



The electrolytic gas was then introduced, and exploded. As the explosion-burette was graduated, the total volume of the gas, as well as that of the residual hydrogen, was read. There were 16.43 c.c. of gas; the residual hydrogen measured 1.01 c.c. at normal temperature and pressure, and thus amounted to 6.18 per cent of the total. The volume of this gas was increased by lowering the pressure so that it was in contact with the fused potash. It was left for more than an hour; the potash, of course, was wet with the water formed by the explosion.

The capillary tubes above the stop-cock of the gas-burette, which had been twice washed out with oxygen, were pumped as empty as possible, until the vacuum-tube showed only the yellow and green lines of the mercury spectrum and the faintest trace of a hydrogen spectrum. A strong current was passed between the electrodes so as to heat them and expel occluded oxygen. After this process had been repeated as long as was thought safe, until, as remarked, the hydrogen spectrum was extremely faint, the tap to the pump was closed. The hydrogen containing the emanation was then admitted from the explosion-burette; it was dried by passage through the narrow tube A filled with phosphoric anhydride, and it entered the bulb C,

* A Paper read before the Royal Society, May 19, 1904.

and the vacuum-tube D. This vacuum-tube was made of lead-glass, with electrodes of aluminium. It was 2.5 c.m. long, with a capillary of about 1 c.m. in length. The aluminium electrodes were closely surrounded with glass, fused round them, so as to limit the capacity of the tube as much as possible; it was probably under one-twentieth of a c.c.

Liquid air was next poured into the jacket surrounding the bulb C, and the reservoir was raised and lowered half a dozen times, so as to convey all the gas into contact with the cooled bulb. The mercury was then raised to the level *a*, and the tap to the pump opened; and while the jacket was kept replenished with liquid air the hydrogen was pumped off until its spectrum had almost entirely disappeared, the red line being hardly visible. The tap to the pump was then closed, the level of the mercury was raised to *b*, and the liquid air allowed to evaporate. The bulb was so bright that it was easy to read the time on a watch. The mercury was then raised to the level *c*, and the current passed. The spectrum was very brilliant, consisting of very bright lines, the spaces between them being perfectly dark; it had a striking resemblance in general character to the spectra of the gases of the argon group.

A direct-vision spectroscopic, made to special design by Heele, with an illuminated scale for reading, had immediately before been standardised by noting the position of the leading lines of helium and hydrogen. They were found to lie exactly on a scale which had previously been constructed. The new lines were read as rapidly as possible, an operation which required about half a minute. During a second reading many of the lines had faded, and the secondary spectrum of hydrogen began to appear, and rapidly grew stronger. It was identified by throwing into a field a hydrogen spectrum through the small prism; and it soon became so powerful as to mask the spectrum of the emanation completely. In order to attempt to recover it, the mercury was again drawn down to *a*, and liquid air again poured into the jacket; the emanation again condensed, and the tap to the pump was opened, and the hydrogen removed by the pump until its spectrum was again hardly visible. On repeating the series of operations already described, the spectrum of the emanation was seen a second time, but it was so transient that only the position of some of the lines could be confirmed.

Next day, only the spectrum of hydrogen was visible; its secondary spectrum was strong. The day after, the same was the case; but interposing a jar and spark-gap brought out two lines which had previously been mapped; they were very feeble.

In the table which follows, all the strong lines which were read are given; the degree of coincidence of those which are of known wave-length shows the approach to accuracy obtained; the error is probably less than five Angstrom units.

Wave-length.	Remarks.
6567	Hydrogen C; true wave length, 6563; observed each time.
6307	Observed only at first; evanescent.
5975	" " "
5955	" " "
5805	Observed each time; persistent.
5790	Mercury; true wave-length, 5790
5768	" " " 5769
5725	Observed only at first; evanescent.
5595	Observed each time; persistent and strong.
5465	Mercury; true wave-length, 5461.
5105	Not observed at first; appeared after some seconds; persisted, and was visible during the second examination.
4985	Observed each time; persistent and strong.
4865	Hydrogen F; true wave-length, 4861.
4690	Observed only at first.
4650	Not observed when the emanation was examined again.
4630	Ditto.
4360	Mercury; true wave-length 4359.

When the spectrum was examined two days later, besides the hydrogen and mercury lines, there were seen:—5595, feeble; 5105, feeble; 4985, very feeble; this was with a jar and spark-gap interposed; the ordinary discharge showed only the primary and secondary spectra of hydrogen, and that of mercury.

Eleven days later, the emanation from the same stock of radium bromide was collected, and treated in exactly the same manner. This time, however, an excess of conscientiousness made us continue to extract gas with the pump from the bulb C containing the frozen emanation, surrounded by liquid air, for too long a time. Every two or three strokes of the pump collected a minute bubble, occupying about the tenth of a millimetre in length of the very narrow fall tube of the pump, which was really a fine-bore capillary. The yield of gas appeared to be continuous; and when these bubbles were examined in the dark they were brilliantly luminous. This gas was really the emanation, which possesses a feeble vapour pressure even at the temperature of liquid air. Needless to say, on attempting to examine the spectrum, little was seen, for the pressure of gas in the vacuum-tube was too low.

The tube was therefore washed out with the gas which had been pumped off, and the process was repeated. The minute bubbles which passed down the capillary fall-tube of the pump were examined, and pumping was stopped when they showed a very faint luminosity in the dark. On compressing the emanation into the spectrum-tube, the spectrum was again brilliant, and measurements were made. It was found possible to read the lines several times, for although the spectrum faded in less than a minute, it appeared to recover on ceasing to pass the current. But this recovery soon failed, and, as before, nothing could be detected after five minutes but the primary and secondary spectra of hydrogen. Now the tube was practically vacuum before warming the bulb containing the emanation; no current would pass; but it is, of course, possible that the gas carrying the emanation had not been perfectly dried in passing through the tube B, containing phosphoric anhydride; any water-vapour would have condensed in the cooled bulb C, and would only slowly have vapourised into the vacuum-tube. On arriving there, it would give the hydrogen spectrum. Another possibility is that it may have come out of the electrodes; for it has been frequently noticed in glowing out a vacuum-tube with aluminium electrodes, that even after all trace of hydrogen has been removed by passing the discharge so as to heat the electrodes, and by pumping, the hydrogen spectrum has re-appeared on admitting a trace of one of the gases of the argon group, and passing the discharge for a longer time; but the intensity of the spectrum which replaced that of the emanation may perhaps warrant the supposition that hydrogen as well as helium is one of the products of the disintegration of the emanation. This, however, is very doubtful, and judgment may be suspended until more satisfactory evidence is forthcoming.

The lines read were:—

Wave-length.	Remarks.
6359	Not observed before; faint.
5975	Observed before; faint.
5955	" " "
5890	Not observed before; faint.
5854	" " "
5725	Observed before; fairly strong.
5686	Not observed before; faint
5595	Observed before; strong and persistent.
5580	Not observed before; faint.
5430	" " "
5393	" " "
5105	Bright; persistent; observed before.
4985	" " "
4966	Not observed before; bright, but transitory.
4640	Transitory; possibly 4650 and 4630, as were seen before as distinct lines.

The line 4966 was particularly brilliant at first; but it soon assumed secondary importance. Some lines which had previously been observed were not seen; they are 6307, 5805, 5137, and 4690. An attempt was made to obtain the spectrum with a jar and spark-gap; but only hydrogen and mercury were to be seen. The resistance soon became very high, and there was danger of piercing the vacuum-tube.

Previous attempts in conjunction with Mr. Soddy gave lines with wave-length 5725 (jar), 5595 (no jar), 5105 (no jar), 4985 (no jar); the line 5585 was observed three times, and 5105 twice previously. The lines 6145 and 5675 mentioned in our last paper (April, 1904) were not seen unless the latter is identical with 5580. It may perhaps be mentioned that the line 5595 was seen by Pickering in the spectrum of lightning, and was not identified with a line in the spectrum of any known gas; it is said to have been a very strong line, of intensity 30 (*Astrophysical Journal*, 1901, vol. xiv., p. 368).

There can be no doubt that the lines given are the chief lines in the visible spectrum of the emanation; as for the pressure, the volume of emanation was about $1/30,000$ th of a c.c., and the capacity of the vacuum-tube, say, $1/20$ th; this would make the pressure about $1/10$ th of a millimetre. It may have been twice as much, for the numbers given are merely estimates.

It may be remembered that, at the Chemical Congress held in Paris in 1900, it was suggested that no element should receive a name until its spectrum had been mapped. Of course, the converse does not follow that, after the spectrum of an element has been mapped, it should receive a name. The "emanation from radium," however, is a cumbersome expression, and sufficient evidence has now been accumulated that it is an element, accepting that word in the usual sense. It is true that it is only a transient element, and ought in justice to be called a compound; but of what? It stands on a wholly different plane to any known compound in the amount of heat with which it parts during its spontaneous change, and in the peculiar electrical phenomena which accompany its transformation. It is a gas; it follows Boyle's law; as Rutherford and Soddy have shown, it resembles the gases of the argon series in its indifference to chemical reagents, for it not merely withstands the prolonged action of magnesium-lime, at a red heat, but also, as Ramsay and Soddy have proved, prolonged sparking with oxygen in presence of caustic potash. Its molecular weight has been found to be nearly 200, and, if it is monatomic, that number would also express its approximate atomic weight. Now, it appears advisable to devise a name which should recall its source, and, at the same time, by its termination, express the radical difference which undoubtedly exists between it and other elements. As it is derived from radium, why not name it simply "exradio"? Should it be found that the emanation, which is supposed to be evolved from thorium, is really due to that element, and not to some other element mixed with thorium in exceedingly small amount, a similar name could be given, namely, "exthorio." If the existence of actinium as a definite element is established, its emanation would appropriately be named "exactinio." It is unlikely that others will be discovered, but, if they are, the same principle of nomenclature might be applied.

It should be stated, in conclusion, that Mr. Soddy collaborated in the experiments preliminary to this successful mapping of the spectrum; had he not been obliged to leave England, he would, no doubt, have shared whatever credit may attach to this work.

A VOLUMETRIC METHOD FOR THE ESTIMATION OF MERCURY FULMINATE.

By HENRY W. BROWNSDON, B.Sc., Ph.D.

THE use of sodium thiosulphate solution as an agent for decomposing fulminate of mercury was first brought to my notice by Mr. George Smith, manager of Nobel's Fulminate Factory at Polmont, and with a view to its adoption in this laboratory I have had the opportunity of making an inquiry into the nature of the reaction. My work in this direction is, however, still incomplete, and I now only wish to mention an analytical application which has resulted as a side issue.

When fulminate of mercury is decomposed by excess of sodium thiosulphate solution, the resulting solution reacts alkaline, and the determination of the amount of alkali thus formed affords an easy and quick volumetric method for the estimation of mercury fulminate.

Method.—The only solution required is one of sulphuric acid approximately N. 10. This is standardised as follows: 0.04 to 0.05 gm. of pure mercury fulminate—prepared by dissolving the ordinary commercial product (1 mol.) in pure potassium cyanide (1 mol.) solution, precipitating the mercury fulminate from the solution of the double salt by means of dilute nitric acid, washing several times by decantation, and finally on the filter-paper till quite free from acid, and then drying at 80 to 90°—is weighed out into a 100 c.c. flask containing about 50 c.c. water; 1 gm. of pure sodium thiosulphate is then added, the flask well shaken till all the fulminate has dissolved, and then made up to the 100 c.c. mark. Portions of 25 c.c. are withdrawn by means of a 25 c.c. pipette, and titrated with acid after addition of one drop methyl orange. It is well to allow the acid to drop from the burette drop by drop, shaking the liquid to be titrated all the time, so that no portion of the liquid becomes locally acid.

The above is repeated on three separate weighings, and the mean taken. The value of 1 c.c. H_2SO_4 in grms. of fulminate is thus obtained.

As applied to the determination of mercury fulminate in cap or detonator compositions, one precaution is necessary, viz., that the amount of fulminate in the weighed out portion of composition should not exceed 0.05 gm., otherwise the results will tend to be low on account of the alkali set free reacting with the finely divided antimony sulphide. For a cap composition containing 15 to 20 per cent fulminate, a weighing of 0.25 gm. is suitable, whilst for a detonator composition containing 35 to 40 per cent fulminate a weighing of 0.12 gm. is sufficient.

The above amount of either cap or detonator composition is weighed out into a 100 c.c. flask containing about 50 c.c. water, 1 gm. of pure sodium thiosulphate added, and the contents well agitated till one is sure all the fulminate has been decomposed (one and a-half to two minutes). The flask is then filled up to the 100 c.c. mark, the contents mixed, and filtered through a dry folded filter-paper into a dry flask. The first runnings are returned through the filter-paper till the filtrate is clear. Portions of 25 c.c. are then titrated as above. To ensure accuracy, a rough preliminary experiment is made, and then two subsequent determinations on two separate weighings, taking the mean of the two latter for the result.

The solutions must not be allowed to stand, but must be titrated as soon as possible after the addition of the thiosulphate, since after a time secondary reactions set in which neutralise some of the alkali giving low results.

Following are a few typical results obtained by applying this method to compositions containing a known weight of fulminate.

By careful working it is possible to estimate the weight of fulminate to within ± 0.0001 gm., an error which is less than 0.1 per cent when calculated out for the percentage of fulminate in the composition. I am continuing this work, and hope shortly to give a fuller account of the reaction

Technological and Scientific Dictionary.—Part III. of this Dictionary has just been issued by the publishers, George Newnes, Ltd. We have previously referred to the merits of this work, of which the present number comprises those subjects coming between C O P (Copper losses, *Elect. Eng.*), and E L E (Electric lighting), the pages running from p. 129 to p. 192.

Weight of fulminate taken.	Weight of Sb_2S_3 .	Weight of KClO_3 .	H_2SO_4 (1 c.c. = 0.00832 grm. fulminate).		Weight of fulminate found.
			First titration.	Second titration.	
Grm.	Grm.	Grm.	C.c.	C.c.	Grm.
0.0328	0.05	0.05	1.00	0.98	0.0329
0.0483	0.05	0.05	1.45	1.45	0.0482
0.0462	0.05	0.05	1.40	1.38	0.0462
0.0425	0.10	0.10	1.25	1.30	0.0424
0.0458	0.10	0.10	1.35	1.40	0.0457

along with its bearing on the composition of the fulminates, a point on which the decomposition by thiosulphate and by sodium sulphide seems to throw much light.

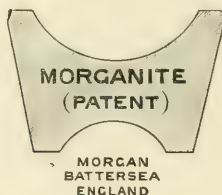
I have much pleasure in acknowledging here the kindness of the directors of the Kings Norton Metal Company, Limited, who have placed facilities at my disposal for carrying out this work.

A NEW MAGNESIA CUPEL.

THOSE of our readers who employ magnesia in preference to the bone-ash cupels which have for so long held the field, will be interested in an ingenious improvement which has recently been made in the Morganite cupels introduced by the Morgan Crucible Company, of Battersea.

Although the numerous advantages possessed by magnesia cupels as compared with those of bone-ash are now generally recognised, the slightly slower absorption of the litharge by the former tends to permit a portion of the litharge to soak down through the bottom before it can diffuse into the body of the cupel. Hence, before the cupels are fully saturated, a portion of the litharge is lost, and the muffle may become corroded by the litharge. The former is usually of little consequence, and the latter may be obviated by the practice which many assayers adopt, of keeping a layer of bone-ash, magnesia, or other absorbent in the muffle, but both are practically abolished by use of the new cupel.

The improvement, as shown in the accompanying sketch, consists merely in making the cupel with a cup-shaped depression in the bottom; in fact, in making it double ended. The litharge soaks through exactly as in



ordinary cupels, but as the middle portion is not in contact with the muffle floor, it has time to diffuse into the body of the cupel before it accumulates sufficiently to actually escape at the bottom.

This simple device has been found to answer all expectations. It permits of the cupellation of a larger quantity of lead per cupel without loss of litharge, and it is stated by the inventors that cupellation progresses more rapidly in these than in the old form of cupel.

As we presume that these cupels will not cost more than the old form, it may be worth while for our readers to try them and ascertain how far their experience bears out the statements of the inventors as to the results which they have obtained in practice.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1904.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, June 8th, 1904.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 204 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 204 samples examined by us during the month, all were clear, bright, and well filtered.

There has been a large excess of rain during the month of May. The actual rainfall measured at Oxford during the month was 3.20 inches, and the average fall is 1.75 inches; thus we have an excess of 1.45 inches, which, if added to the previous excess of 0.98 inch, makes a total of 2.43 inches, or 27.9 per cent above the average for thirty-five years.

Our bacteriological examinations of 370 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 364 others from special wells, standpipes, &c., making 734 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	116
New River, filtered (mean of 74 samples) ..	4
Thames, unfiltered (mean of 25 samples) ..	4120
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 196 samples) ..	15
Ditto ditto highest	181
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	225
River Lea, from the East London Water Company's clear-water wells (mean of 25 samples) ..	19

Of the 295 daily samples taken from the general filter wells of the Metropolitan Water Companies, twenty-two samples, or 7.4 per cent, were sterile. Five samples, or 1.6 per cent, contained more than 100 microbes, and of these, two samples contained more than 150 microbes per c.c. The five excess samples contained an average of 143 microbes per c.c. In April five excess samples contained an average of 123 microbes per c.c.

From the above figures it will be seen that the high condition of purity observed during April has been well maintained during the month of May, in spite of the great increase of rainfall.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

INTERNATIONAL ATOMIC WEIGHTS.*

By JOJI SAKURAI and K. IKEDA.

Science College, Imperial University,
Tokyo, Japan, May 10, 1904.

To the Editor of the *Chemical News*.

DEAR SIR,—I am sending to you by this mail a copy of the reprints of a letter addressed by my colleague Prof. Ikeda and myself to Professor F. W. Clarke on the subject of International Atomic Weights. Although the letter, which forms a part of our report to the Tokyo Chemical Society on International Atomic Weights, has been printed in the *Journal* of that Society, I shall be obliged if you can find space for its publication in your valuable journal, knowing that hundreds of the readers of the *CHEMICAL NEWS* take interest in the subject, and that the *Journal of the Tokyo Chemical Society*, which is printed in Japanese, is quite closed to the scientific world.—I am, your obedient Servant,

JOJI SAKURAI.

The following letter was addressed by us to Professor F. W. Clarke on the subject of International Atomic Weights:—

Tokyo, Japan, March 28th, 1904.

Professor F. W. CLARKE, Chairman of the Sub-committee on International Atomic Weights.

DEAR SIR,—Whilst we wish to tender our sincere thanks to you and your worthy colleagues for the laborious task of yearly reviewing and compiling the table of atomic weights for international use, we feel at the same time bound to make some observations upon the course you have adopted in prosecuting the work entrusted to you.

The first and most important point is in reference to the introduction of the double standard. We can appreciate the delicate position which you occupy with respect to this much-controverted question, and we can also understand why you chose to leave the matter to take its own course without giving decision in one way or the other. But, as you must know, the larger committee on International Atomic Weights, from which the sub-committee has been formed, had decided, by a great majority of votes, to use *exclusively* those atomic weights which are based on the oxygen standard. The introduction of the double standard is therefore utterly against the above decision, and also in direct opposition to the very motive with which the International Atomic Weights Committee has been organised; moreover, the matter has thereby become worse than ever, for there are now two sets of atomic weights which are apparently equally authorised.

But, apart from the question of the previous history which the formation of the Sub-committee possesses, and which, as it appears to us, you have wholly disregarded, we beg to call your attention to the following circumstances:—

In looking over your tables of atomic weights for 1903 and 1904, we observe that, in the numbers under $O = 16$, only so many figures are given that the last figure may also be taken as correct. That you deem the adoption of this rule, which had been adhered to by the German Committee, desirable is evident from the remark you have made with respect to $H = 1.008$ in your Report for 1903, but when we examine the atomic weights under $H = 1$ we find curious contradictions. The atomic weight of oxygen is given with only four figures—that is, $O = 15.88$ —from which we may conclude that you regard the ratio $O : H$ has been only so far determined with certainty, and not further, and we are consequently at a loss to understand how the atomic weights of iodine, lead, and silver have been evaluated to five figures, as given. Professor Morley's ratio, $O : H = 15.879$, has apparently been employed for the purpose; but then, in accordance with the principle which

made you alter $H = 1.01$ to $H = 1.008$, the atomic weight of oxygen should stand as $O = 15.879$, and not $O = 15.88$, as in your tables. This, it appears to us, illustrates in the most conspicuous manner the shortcomings of the hydrogen standard, which have already been pointed out by various chemists.

Again, on going through your tables, one is tempted to entertain the absurd notion that the atomic weights according to the hydrogen standard could be ascertained with greater accuracy than those based on the oxygen standard, for there are as many as eighteen elements whose atomic weights have more figures under $H = 1$ than under $O = 16$, while there is only one element treated in the opposite manner. Of these eighteen elements thus favourably (?) treated under $H = 1$, the majority are rare elements, whose atomic weights are avowedly less accurate than the others. What is more remarkable still is the fact that one finds phosphorus among the number—an element whose atomic weight, according to your Report, "has been peculiarly neglected." It is clear that you do not have much confidence even in the value $P = 31.0$ ($O = 16$). What sort of reliance can, then, be placed in the last figure of the value $P = 30.77$ given under $H = 1$? Are these contradictions mere consequences of re-calculation of the atomic weights under $H = 1$ from those under $O = 16$? Or are there some other reasons for the adoption of these values?

However it might have been, the lack of uniformity in the two series is lamentable. This is only one of the unhappy consequences of retaining both standards. It might perhaps be urged that the uniformity in the treatment of figures can be ensured by taking ordinary critical care in re-calculation; but the fact that such re-calculation, which, moreover, involves the uncertainty of the ratio $O : H$, is at all necessary, is a great drawback of the hydrogen standard.

As Professor Ostwald strongly protested against the adoption of the hydrogen standard directly after the appearance of your first Report, we have been waiting for the publication of your second Report in the hope of seeing it dropped. But our hopes have been denied, and we feel ourselves obliged to address this letter to you.

There is another matter which, though of less importance, cannot be allowed to pass unnoticed, namely, the alteration of the symbols Be for beryllium and Nb for niobium into Gl (glucium) and Cb (columbium) respectively, which has been introduced into your tables. That atomic symbols ought to be as much international as atomic weights has been well recognised in the use, for example, of the symbol K for potassium. There is nothing which prevents the use of one name for an element in one country and another name in another, but surely atomic symbols should not be allowed to suffer similar discrepancies. The symbols Be and Nb have been and are most generally employed all over the world; if Gl and Cb had any claim to be considered as candidates, the choice ought to have been made according to the broadest international usage.

Lastly, we would like to call your attention to the unsatisfactory state of the relation which exists between the originally formed larger committee on International Atomic Weights and the Sub-committee of which you are the worthy Chairman—or, rather, non-existence apparently of any relation whatever between the two. Members of the larger committee do not receive any report from you, nor are they told through what periodicals your report will be made known to them. The matter of history has, it appears to us, been again disregarded here.

Trusting that the points represented above may receive your due consideration, and also that we may be allowed to publish this letter,—We are, Dear Sir, your obedient Servants,

K. IKEDA,
JOJI SAKURAI, } Members of the Committee
on International Atomic
Weights, representing the
Tokyo Chemical Society.

* From the *Journal of the Tokyo Chemical Society*, April, 1904.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 10th, 1904.

Dr. R. T. GLAZEBROOK, President, in the Chair.

PROF. H. L. CALLENDAR gave a demonstration of the "Projection of the Indicator Diagrams of a Petrol Motor."

The lantern-slides illustrated the working of the motor under various conditions, and were prepared to elucidate the nature of some of the defects which occur in practice. The motor itself was exhibited in action, with the indicator attached, and the actual diagrams were projected on the screen showing the changes of form as they occur when the conditions of running are changed. The motor employed was a Clement-Garrard cycle-motor, with 60 m.m. bore and 70 m.m. stroke. The inlet valve is automatic, and is provided with an arrangement for varying the tension of the spring for experimental purposes when the engine is running. The indicator used was a Hospitalier-Carpentier manograph, with certain modifications which are necessary for high-speed work. It is connected directly to the cylinder by a short steel tube in place of the long fine copper tube usually employed. The pressure acts on a thin steel disc, the movements of which are communicated to a small pivoted mirror, which is tilted upwards through an angle proportional to the pressure acting on the disc. The movement of the mirror is observed or recorded by a ray of light reflected on to a screen or photographic plate. In order to record the pressure at each point of the stroke in the form of a continuous curve or diagram, the mirror is simultaneously tilted from side to side by a little crank revolving in time with the fly-wheel, so that the spot of light reflected from the mirror moves horizontally in time with the motion of the piston in the cylinder. Owing to the high speed the spot of light is seen as a continuous curve, which is readily measured or photographed. The engine works on the four-stroke cycle of operations—suction, compression, explosion, and exhaust—and runs at speeds varying from 2000 to 2500 revolutions per minute.

Prof. Callendar exhibited a series of lantern-slides showing how the characteristics of the diagram depend upon the point of the stroke at which the gases are ignited. He also demonstrated experimentally how the pressure retardation, which occurs when using a long fine copper tube to connect a high-frequency engine to a manograph, could be compensated by retarding the position of the spot of light relative to the piston by an amount equal to the retardation of the pressure at any given speed. Leakage is a fruitful source of loss of power, but it was shown that it could easily be detected by an examination of the indicator diagrams. A leak shows itself at a loop at the end of the compression-stroke if the spark is retarded, coupled with a rapid fall of pressure during expansion. The effect of overheating of the engine can be well shown by comparing two diagrams taken under similar conditions with the cylinder cold in one case, but hot in the other. The hot cylinder shows the higher compression-pressure and the smaller explosion-pressure, so that the power is diminished for both reasons.

Diagrams were shown to illustrate the effects of back pressure, due to insufficient exhaust lift or to a throttled silencer. The loss of power on this account is not very serious unless the throttling is excessive.

Prof. J. A. FLEMING read a paper entitled "A Model Illustrating the Propagation of an Alternating Current along a Telephone Cable, and a Simple Theory of the same."

Although the mathematical theory of the propagation of alternating currents along lineal conductors having capacity, inductance, resistance, and leakage has been developed by many writers in great fulness, the conclusions

reached by them have not always been readily assimilated by practical engineers, and in some cases unsound theories have been put forward regarding the conditions limiting telephonic speech along wires. The present paper contains an account of a model (exhibited at the meeting) which has been constructed by the author, for the purpose of explaining in a simple manner the physical meaning of the mathematical expressions which are reached in discussing the propagation of alternating currents along a telephone or telegraph cable. The first part of the paper is concerned with a presentation of the elementary theory of the phenomena expressed in terms of complex quantities, which forms a more suitable mode of investigation than the use of ordinary trigonometrical analysis, as the time-element is thereby eliminated. Beginning with the fundamental differential equations for the distribution of potential and current in an element of such a cable when traversed by any current, these are then thrown into the form appropriate when considering simple harmonic currents, and a solution given for the potential and current distribution in the case of a semi-infinite cable, having a simple periodic E.M.F. applied at the end. This solution is of the form $V = Ee^{-\alpha x}(\cos \beta x - i \sin \beta x)$, and it indicates that the potential, V , at any point in the semi-infinite cable has a maximum value which is less than that at the origin, (E), in an assigned ratio, and shifted backwards by an assigned angle in phase. A geometrical interpretation was then given of the above equations, leading to a graphic representation of the distribution of potential in the cable at any moment, and the model shown illustrated the meaning of the above equation and the graphic interpretation of it. The model consists of a steel axis, on which are keyed a number of wooden discs grooved on the edge. These are set on the shaft eccentrically, and the eccentricity of the wheels diminishes in geometrical progression. Each eccentric is shifted backwards in phase compared with its preceding neighbour by an equal angle, and these eccentricities and phase-angles can be varied. Each eccentric wheel is embraced by a long string, the ends of which are attached to metal blocks which can slide up and down on a steel wire. These strings are all of equal length. When the axis carrying the wheels revolves, each block moves up and down with a nearly simple harmonic motion, but the amplitude of that motion decreases from block to block, and, moreover, the phase of the motion of each block is delayed behind that of its next preceding neighbour by an equal amount. Hence, when the axis is turned round, the blocks, of which there are 48, are arranged in a periodic curve of decreasing amplitude, and move up and down in a manner which imitates the propagation of a wave of alternating current or potential along a cable. The paper then proceeds with a discussion of the theory, and a very simple proof is given of Mr. Heaviside's condition for the distortionless propagation of a wave of electric current. The criterion of distortion is then applied in the case of one long submarine cable, and it is shown how far removed such a cable is from being a distortionless cable. The remedies which have been proposed are then discussed, and it is shown that it is hopeless to expect any real advantage merely by bringing the iron armour closer to the cable-conductor, but that a large reward awaits any inventor who can bestow upon a long submarine cable inductance up to 300 or 400 henries per naut, without at the same time increasing much the usual capacity of 0.3 m.f.s. per knot. Allusion is made to Prof. Pupin's investigations concerning the insertion of inductance-coils at intervals along the telephone lines, and the suggestion is made that there is no difficulty in applying this plan to subterranean telephone trunk-lines, and that considerable improvement in the transmission of telephonic speech could thereby probably be effected.

Mr. T. H. BLAKESLEY congratulated the author upon the interesting result contained in his paper, that under a certain critical relationship, among the properties of the cable relatively distortionless waves might take place whatever the frequency. But he thought some other of the

consequences of this relationship might be more simply exhibited in the forms for potential and current,—

$$V = E e^{-\alpha x} \cos(\delta x - pt), \quad I = \frac{E e^{-\alpha x}}{q} \cos(\delta x - pt + m)$$

where—

$$q^2 = \frac{R}{K} \left(\frac{1 + \left(\frac{L}{R}\right)^2}{1 + \left(\frac{C}{K}\right)^2} \right) \quad \text{and} \quad \tan 2m = \frac{(LK - RC)\delta}{RK + LC\delta^2}$$

q is of the nature of resistance, and m is the angle of lag of the current behind the potential, and is constant for all points of the cable. This lag-angle disappears when $LK - RC = 0$, but from the expression for q^2 it is clear that this quantity will be independent of the frequency if $L/R = C/K$, which is again the same condition. Thus the real degradation of current would be the same for all tones, and the conjunction of current and potential, for all points, would be secured by this condition. It would not, however, be easy in practice to fulfil this condition. There was, however, something to be said for keeping both L and K small, as in fact they are in practice. For, looking at the expression for q^2 , it will be seen that it diminishes as the frequency rises if $CR > LK$, and this is true of cables in practice. Hence, though $e^{-\alpha x}$ grows less with rising frequency the resistance q also becomes less, so that the degradation of current is not so great as that implied in the mere increase of α with frequency. Mr. Blakesley pointed out that in operating upon equations 13 and 14 to obtain equations 20 and 21, the quantity $\sqrt{(R^2 + \delta^2 L^2)(K^2 + \delta^2 C^2)}$ could be written in two ways:— $\sqrt{(KR + \delta^2 LC)^2 + \delta^2 (LK - CR)^2}$. The author had chosen the top signs, but interesting results could be obtained by choosing the bottom signs and contemplating the equality of KR and $\delta^2 LC$.

The CHAIRMAN read a letter from Mr. Jacob pointing out that the dielectric resistance of the 1880 Anglo-American Cable, considered in the paper, is much higher, as it lies in the sea, than the figure quoted by the author, which was obtained at 75° F. and atmospheric pressure after 1 min. electrification. The electrification or absorption of the dielectric, however, masked all the effects of the high insulation value. An inductance of 300 or 400 henries per naut was beyond possibility; the inductance should not be of a higher order than one henry per naut.

Dr. FLEMING, in reply, said that the relation between the electrical constants of the cable which gave distortionless transmission was discovered and announced twenty years or more ago by Mr. Oliver Heaviside. All that he (Dr. Fleming) had attempted to do was to simplify and illustrate the proofs of this condition. The employment of complex quantities in the discussion of alternating-current problems led to a considerable simplification of the analysis. As in practice we were only concerned with the maximum or root-mean-square values of the potential and current, the introduction of the time-variable into the equations led to complicated expressions, the physical meaning of which was not readily apparent to most students. All the usual algebraic expressions for current and potential at any point could, however, be readily obtained from the vector equations he had given. As regards the practical realisation of Heaviside's distortionless conditions for submarine cables, the figures given in the paper were merely intended to indicate the remoteness of its possibility. The correction furnished by Mr. Jacob for the insulation resistance of the dielectric when the cable was immersed did not affect the general conclusions, as if the insulation resistance was greater, the departure from the distortionless conditions would be then still greater. He recognised that the "absorption" of the dielectric introduced a factor not taken into account in the mathematical theory. As regards the practical superior limit of inductance which might be given to a cable, no one could say what invention might not bring forth. He was glad

to hear that an inductance of 1 henry per naut might improve matters sensibly, because he had devised a plan by which an approximation to this might be reached. Mr. Jacob only confirmed the statement in his paper in expressing the opinion that an inductance of 300 to 400 henries per naut was impracticable.

Mr. M. E. J. GHEURY then exhibited a Gyroscopic Collimator. The instrument is used in conjunction with an ordinary sextant, the observation being taken as with the sea horizon by bringing the image of an observed body into a field of vision, in which a horizontal grating of a special kind allows the observer to ascertain the direction of the true horizon. The essential feature of the collimator is a gyrostat equivalent to a long pendulum, the period of vibration of which is very much greater than the periods of the various motions of the ship upon which it is used.

THE FARADAY SOCIETY.

An Ordinary Meeting of the Faraday Society was held on Thursday, June 9th, at the Institution of Electrical Engineers. The President, Dr. J. W. SWAN, was in the Chair.

M. ADOLPHE MINET presented the first part of a paper on "*The Electric Furnace, its Origin, Transformations, and Applications.*"

The paper discusses the growth of the furnace from the historical point of view, and then proposes a new classification, which is worked out in minute detail in the form of a table. A full bibliography of the electric furnace completes this section of the paper.

This discussion was postponed until the autumn, when the author will complete his study and fully illustrate his subject.

Dr. F. M. PERKIN described a form of Porous Diaphragm that he has found convenient for laboratory use. It consists of two perforated concentric porcelain cylinders packed in between with brown paper, asbestos, or other material, depending on the use to which the diaphragm is to be put.

Mr. G. T. BILEY read a paper on "*The Hard and Soft States in Metals.*"

The wide range of the phenomena which are directly or indirectly associated with the hard and soft states in metals indicates that a knowledge of these states is of fundamental importance. An exclusively crystalline theory of metal structure, even when stretched to its widest limits is insufficient fully to explain these phenomena. But the crystalline is not the only form of solid aggregate; the movement of the molecules in the liquid state may be so suddenly arrested that they have no time to fall into the regular formation of the crystalline state, so that the solid which results is amorphous, not crystalline. A suddenly congealed liquid may be likened to an instantaneous photograph of the rapidly moving molecules of the liquid state.

The views here advanced are based on the author's earlier observations on surface flow in crystalline solids. The evidence afforded by the micro-structure has been supplemented by observations on the other properties of metals in the hard and soft states, and the view is now advanced that these states are perfectly distinct phases. This is shown by the mechanical, electrical, optical, and thermo-chemical properties as well as by the micro-structure. The soft phase, C, is crystalline, and the hard phase, A, is amorphous.

The transformation of A into C is effected by heat, and takes place at a definite transition-temperature. On either side of the transition-point the various properties are characteristic and distinct; for instance, an E.M.F. of 120 micro-volts may be developed in a thermo-junction of silver in the two phases. The E.M.F. falls to zero after the junction has been heated to 260° for a few seconds. Silver

leaf, which is opaque and highly reflecting below the transition temperature, becomes transparent and very much less reflecting if kept for a time at a temperature a little above that point.

The transformation from hard to soft is thermally irreversible, but is readily effected mechanically. This reverse transformation—soft to hard—takes place when the metal is deformed by over-strain, however slight. It takes place through an intermediate mobile phase in which the molecules have a freedom analogous to that in the liquid phase. This freedom is produced by motion directly imparted to the molecules during the slipping of one portion of the material over another. The state of the mobile phase is somewhat analogous to that of an undercooled liquid. This transformation, C—M—A, while it occurs at every moving surface, does so, as a rule, in extremely thin layers. The layers of the hard phase which result supply a rigid casing for the unaltered crystalline elements, and thereby give a granular and cellular structure to metal which has been overstrained by having any kind of work done on it. The co-existence of the two phases in this way accounts for the variety of structure which may be developed in malleable and ductile metals.

Dr. T. M. LOWRY said that the temperature which Mr. Beilby called the transition-point was not a true *transition-point*, such as exists, for example, in sulphur at $96^{\circ}\text{C}.$, at which the rhombic passes into the monoclinic phase, but really the *stability-limit*; that is, the temperature at which the mobility of the molecules enables a change which has been trying to take place all along to do so at a visible velocity.

Mr. J. C. M. GARNETT suggested that the different results obtained in the two methods—by transmitted and reflected light—of measuring the optical constants might be explained on Mr. Beilby's hypothesis of an A and C phase.

Dr. C. M. DESCH thought that the existence of a thin transparent film on the surfaces of polished metals might explain the Kerr effect.

THE ROYAL SOCIETY.

CONVERSAZIONE AT BURLINGTON HOUSE.

ON Wednesday evening last, June 22nd, a most successful *Conversazione* was held at the Royal Society's Rooms at Burlington House, the occasion being known as "Ladies Night," and the guests were received by Sir William and Lady Huggins.

A certain number of the exhibits were shown at the last *Soirée*, on May 13, and have been already noticed in these columns.

Among the most interesting of those to be seen on Wednesday evening last we may mention a very ingenious instrument, exhibited by Mr. W. DUDELL, called the Thermo-galvanometer, an instrument for measuring very small alternating currents. The instrument is intended for the measurement of very small rapidly-varying currents, such as telephonic currents and the currents produced in the receiving vertical wire in wireless telegraphy. Signals were sent from a transmitter at the end of the main library (Room V.); the very small current produced in the vertical wire at the receiving station was measured with the thermo-galvanometer, and the great increase in the current due to tuning the receiving circuit was demonstrated. Some experiments with telephonic currents were shown. The sensibility of the instrument is such that either direct or alternating currents from a few micro-amperes upwards can be measured. The deflection is practically proportional to the mean squared value of the current flowing.

Mr. W. HIBBERT showed a new Magnetic Balance, constructed as follows:—The beam of a balance is made of a magnetised steel rod 27 c.m. long. The "centres" of the poles are 25 c.m. apart. The repellent pole of a second

magnet being placed over one end of the beam causes this to descend, and the force of repulsion is balanced by a weight sliding on the other half of the beam. The absolute value of a pole in C.G.S. units can be ascertained in a very few minutes, without reference to the terrestrial or other field. The instrument can also be used for finding the approximate value of an electric current.

A simple method for printing without the use of inks was shown by Mr. FRANCIS SHERIDAN called the *Physiotype*. It is specially adapted to finger printing and the reproduction of designs from animal and vegetable life. The subject to be reproduced is pressed on paper, and an invisible impression is developed with a coloured powder into a dark and permanent print.

The Cilioscrite, exhibited by Dr. W. E. DIXON and Mr. O. INCHLEY, is a machine to record the movements of cilia and the effect of physical conditions and chemical reagents upon them. The apparatus consists of an upright silver rod free to revolve on its vertical axis. A light aluminium wheel is fixed to the upper end of this and a short ebonite spindle a few centimetres lower, all having the same vertical axis. The ciliated mucous membrane from the frog's pharynx is wrapped round the spindle. Hooks are fixed into the ends of the membrane and connected to a silk thread which passes over a pulley to a weight. The cilia turn the spindle, and a record of their activity is obtained by a time marker recording seconds on a blackened paper attached to the aluminium wheel.

Mr. C. E. S. PHILLIPS showed an Automatic Vacuum Pump of novel construction. The apparatus consists of a modified Toepeler pump, so arranged that it works automatically through the operation of electrically controlled devices, for the purpose of producing extremely high rarefactions. The pump will reduce the gas pressure within a vessel of 200 c.c. capacity from that of the atmosphere to 0.002 m.m. in fifteen minutes. By the action of the mercury in completing the circuit of a relay a solenoid is excited which operates a four-way slide valve, and this, in its turn, connects the lower chamber of the Toepeler pump with either the atmosphere or a mechanical pump, depending upon whether the mercury touches the lower contacts or those in the air trap on the left hand side of the apparatus. Particular attention is drawn to the adjustable device for causing the mercury to pause before ascending into the upper chamber.

Mrs. AYTON showed some striking experiments on the Origin and Growth of Ripple Marks. The experiments illustrate the way in which the sand ripples are formed on the sea shore. If sand be spread quite evenly on the bottom of a trough, and water above the sand be oscillated so as to produce stationary waves, a small ridge is formed where the horizontal velocity of the water is greatest, next a ridge is started on each side of the first, which grows; then two more ridges are started, the former growing, and so on until the whole surface of the sand is ripple-marked. Each ripple now slowly moves towards the place of greatest horizontal velocity, while fresh ripples from near the places of least horizontal velocity. Pairs of ripples then coalesce here and there, and finally the greater part of the sand is assembled in a ripple-marked heap at the places of greatest horizontal velocity, this final result being attained, for example, in about twenty-five minutes in the case of the six foot trough exhibited, when the stationary wave is twice the length of the trough. The vortices which are produced in the lee of each ridge during a part of each swing of the water are shown by means of pepper, and the way in which these vortices build up the ridges is exhibited.

During the evening the following demonstrations were given, with Lantern illustrations:—

Lantern Slides, illustrative of—(1) Operations at the Simplon Tunnel; (2) The Victoria Falls and Gorge of the River Zambesi, and proposed Bridge, by Mr. FRANCIS FOX.

The Charge of Negative Electricity fired off by Radium, by the Hon. R. J. STRUTT.

Colour Photographs of Living Insects, by Mr. F. ENOCK, F.L.S. This last lecturette was of great interest. By no other means than that of colour photography would it be possible to reproduce the natural colours of living insects and their environment. The protective colouration and markings, as well as the natural pose of the insect, are all brought out in a marvellous manner. Insignificant markings, when seen from different points of view, are shown to be of the highest importance for the protection of the insect.

NOTICES OF BOOKS

Radio-activity. By E. RUTHERFORD, D.Sc., F.R.S., F.R.S.C., Macdonald Professor of Physics, McGill University, Montreal. London; C. J. Clay and Sons.

In this book, dedicated to "J. J. Thompson as a tribute of respect and admiration," the author has endeavoured to give a complete account from a physical standpoint of the properties possessed by the naturally radio-active bodies. As our knowledge of radio-activity has been obtained chiefly from information gained by research into the electric properties of gases, this latter subject is rather fully discussed, and a valuable chapter is included giving the various forms of apparatus used, and the methods for the measurement of radio-activity generally in use. The book constitutes a complete summary of the work that has been done upon this very interesting subject, and although some readers may not be prepared to accept at once all the speculations and hypotheses set forth, it is both interesting and valuable to have a clear statement of the grounds upon which have been based some of the most startling conclusions of recent times.

The ionisation theory of gases and the part it has played in furnishing a satisfactory explanation of the passage of electricity through vacuum tubes is discussed in Chapter II., where also the measurement of radio-activity by the determination of the "saturation current" is fully described, as are also C. T. R. Wilson's experiments on the condensation of water upon nuclei, and the use they have been put to by Prof. J. J. Thompson in his recent researches, forming as they do links supporting the series of interesting speculations that are now woven round the phenomena of radio-activity.

In Chapter III., "Methods of Measurement," the action of the rays upon a photographic plate, though valuable as a means of investigating the curvature of the path of the rays where deflected in a magnetic field and similar phenomena, is open to many restrictions as a means of general investigation, and the electric methods for the measurement of the "saturation current" is to be preferred. Various forms of electrosopes are described; one very useful form used by M. and Mme. Curie in their earlier researches is illustrated in full; with this instrument comparative tests of the radio-activity of various materials can be rapidly made, but it is not suited for absolute measurement. A modified form of electroscope has recently been devised by Mr. C. T. R. Wilson that is likely to be very useful. It consists of a small rectangular brass box containing at one of its ends a brass plate insulated and maintained at a constant potential of 200 volts; through the opposite side of the box a wire carrying a very narrow gold-leaf is fixed, insulated by a sulphur bead; normally the gold-leaf is attracted to the charged plate, and the box is tilted to the angle of maximum sensitiveness, about 30°. The other end of the wire carrying the gold-leaf is connected to the insulated system whose rise or fall of potential is to be measured; a movement of 200 scale-divisions was obtained by a rise in potential of only one volt above the case.

The construction and method of using electrometers is very thoroughly set out, and the chapter concludes with a description of M. Curie's quartz piezo-electric, an instru-

ment little known on this side of the Channel, but one that is particularly adapted to the measurement of saturation currents.

Chapter IV. plunges boldly into the nature of the radiations; α -, β -, and γ -rays are each discussed separately in great detail; a description is given of Mr. Strutt's ingenious apparatus for demonstrating that a radium compound acquires a positive charge if contained in an envelope sufficiently thick to absorb the α -rays, but thin enough to allow most of the β -rays to escape, and also an account of Sir William Crookes's spintharoscope for rendering visible the impacts of the α -rays.

Chapters V. and VI., deal with the rate of emission of energy and the properties of radiation; the effect of radium in causing a spark to pass an alternative spark gap and its effect upon selenium are mentioned, as are also its action upon liquids and some of its chemical properties. Several chapters are devoted to the fundamental experiments that make the foundation of the disintegration theory. It is well that the author's views on this important subject have been clearly set out, and this section of the work deserves very careful study by any who may have been startled by the boldness of the views recently propagated. The physiological action of radium rays and their action upon certain microbes is of interest, being fraught with great possibilities. Sir William and Lady Huggins made the discovery that the light from a phosphorescent radium compound in air shows the line spectrum of nitrogen which can be photographed if sufficiently long exposure is given; this shows that radium at ordinary temperatures is able to set up radiations that are otherwise only produced by the electrical discharge under special conditions. Chapter X. deals with the law of decay and recovery of radio-activity in emanating substances; the theory of radio-active change is elaborated on pages 323-331, including the author's diagrams illustrating the course of alteration in uranium, thorium, and radium, and a full account is given of the experiments of Prof. Sir W. Ramsay and Mr. Soddy upon the production of helium from radium and radium emanation.

The book may be truly said to contain all that is known about the radio-active elements, as well as setting out clearly the very interesting though perhaps revolutionary theories that have been devised to account for their remarkable properties, and it is likely for some time to come to be regarded as the standard work upon the subject.

The Extra Pharmacopœia of Martindale and Westcott.

Revised by W. HARRISON MARTINDALE, Ph.D., F.C.S., and W. WYNN WESTCOTT, M.B., D.P.H. Eleventh Edition. London: H. K. Lewis. 1904. Pp. 809.

SINCE the publication of the tenth edition of the "Extra Pharmacopœia" three years ago, William Martindale, the originator of the book, has passed away, and the revision of the work was entrusted to his son, W. Harrison Martindale, and Dr. W. Wynn Westcott.

In this edition many of the older drugs, chemicals, and preparations have been omitted, thus enabling the revisors to add more than three hundred new remedies, drugs, &c. The size and weight of the volume have been decreased, though it contains 112 pages more than the last edition, by using finer paper, without impairing the clearness of the type.

One important addition is the section on Radiology, in which are introduced for the first time notes on radium, Röntgen rays, high-frequency currents, the Finson lamp, and radiant heat in their important applications to therapeutics. Similar fresh monographs appear on amygdala, colchicum, lecitith, ptomaines, &c., and the section on Mineral Waters contains information of about 150 mineral waters in various parts of the world. The water analysis notes and bacteriological notes have been revised and corrected up to date, and notes on the examination of stomach contents appear for the first time. The index has been revised and re-arranged, internal remedies being

printed in Roman type, while those for local or external use are in italics.

Subject-list of Works on Electricity, Magnetism, and Electro-technics in the Library of the Patent Office.
London: Darling and Son, Ltd. 1904. Pp. 286.

THIS subject-list is No. 14 of the Patent Office Library series, and comprises 2374 works, representing 3792 volumes. The catalogue entries relating to these works number 2918, and are distributed under 307 headings and sub-headings. As an example of the system adopted, if a searcher requires information on Electro-plating of gold and silver, for example, the subject of Electro-plating will be found in the general alphabet under that heading. Further information will be obtained by referring to the key in which the headings are shown in class order. Here he will find the headings "Electro-plating," "Electro-deposition," "Electro-chemistry, Technology of," &c., which should next be consulted.

Immune Sera; Hæmolysins, Cytotoxins, and Precipitins.
By Prof. A. WASSERMANN, M.D. Authorised Translation by CHARLES BOLDUAN, M.D. First Edition.
London: Chapman and Hall, Limited. New York: John Wiley and Sons. 1904. Pp. 77.

THE subject of immunity and the reactions which take place when the blood of one animal is injected into the body of another are matters of interest, and are now becoming also of great importance.

At first these experiments, like so many others, were of scientific interest only, but they have been followed up and observed with such minute care that the results have been found applicable to many clinical questions, as well as to certain other problems of every-day life.

In this book we find described in the clearest manner the results of a large number of experiments by which the author hopes to introduce to his readers the essentials of the subject.

The bulk of the experiments herein described have to do with the injection of the blood or serum of one animal into the body of another, and the first important fact noticed in this connection was the following:—That if horses were injected with red blood cells of rabbits, the serum thereafter obtained from the horses would have acquired an appreciable toxicity for rabbits, and it was found further that this toxic action was really a dissolving power acquired by the horse serum for the red corpuscles of the rabbit. From these early observations the author and others have built up what is practically a new branch of biological science, and which is, moreover, leading up to important results bearing on artificial immunity from infectious diseases.

After it had been found that injection of an animal with red blood cells of another animal was followed by the production of definite specific reaction substances, investigators experimented to see whether this was also the case if other animal cells were used, and it was found that a series of reaction substances resulted, entirely analogous to the hæmolysins obtained from the red blood cells; these sera have been called cytotoxins, and are specific for the cells used for injection.

Another class of bodies are called precipitins, and they develop in the serum by treating an animal with albuminous bodies of another animal, and precipitate these albumins when the sera of the two animals are mixed. This power has been found to be very extensive, but it is not entirely specific; for instance, the serum of rabbits injected with chicken serum is a precipitin, not only for chicken serum but also for that of pigeons; while the serum of rabbits treated with that of guinea-pigs is a precipitin also for the serum of monkeys. The author, however, has elaborated a method for distinguishing the albumins from one another, and particularly to distinguish those derived from man from those of other animals. The reaction is

specific except that the serum of an animal treated with human serum reacts also with the serum of monkeys, but not with that of any other animals so far investigated. The book is one of great interest, and we recommend it cordially.

OBITUARY.

THOMAS BAYLEY.

WE regret to announce the death, on June 7th last, from cardiac failure, of Mr. Thomas Bayley.

Mr. Bayley was the compiler of the well-known "Chemists' Pocket-book," by which work he was best known. He was, however, devoted to original research, which he pursued with unflinching ardour in such time as was available to him from his work as a manufacturing and consulting chemist. His work lay chiefly in the domain of the Periodic Law, and he published several papers in the *CHEMICAL NEWS*, *Journal of the Chemical Society*, *Philosophical Magazine*, and *Journal of the American Chemical Society*. Several new and important relations were laid bare in the course of these investigations, especially one deduced graphically from the At. Vol.-At. Wt. diagram. The result is a power of really accurate prediction of the properties of unknown elements, which has been verified in several important cases.

Mr. Bayley was also the author of "A Pocket-book for Pharmacists," and of "The Assay and Analysis of Iron and Steel, Iron Ores, and Fuel"—a work now out of print, but still in demand. H. S. H.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 21, May 24, 1904.

γ -Diphenylanthracene and Symmetric γ -Diphenylanthracene Dihydride.—A. Haller and A. Guyot.—The authors prepare γ -diphenylanthracene in a pure state, and various derivatives of this body.

Direct Hydrogenation of Homologues of Aniline.—Paul Sabatier and J. B. Senderens.—For the amines of the first group (methyl- or ethylanilines) hydrogenation can be effected by means of nickel between 160° and 180°, and takes place quite regularly. The production of condensed amines, which takes place in the case of aniline, is impossible for the tertiary amines. The only secondary reaction being the production of a little formic amine and benzene, transformed itself into cyclohexane. Ethylaniline, $C_6H_5NHC_2H_5$, gives cyclohexylethylamine, $C_6H_{11}NHC_2H_5$; Diethylaniline, $C_6H_5N(C_2H_5)_2$, giving cyclohexyldiethylamine, $C_6H_{11}N(C_2H_5)_2$; and dimethylaniline, $C_6H_5N(CH_3)_2$, giving cyclohexyldimethylaniline, $C_6H_{11}N(CH_3)_2$.

Thermic Ionisation of Saline Vapours.—G. Moreau.—When saline vapours are raised to a high temperature—say, 1000°—they become conductors, and remain conducting down to ordinary temperatures. The conductivity depends on the nature of the salt and its chemical constitution. The author's experiments on this subject show—
(1) For a solution of constant concentration of a salt, A, the current, i , at first proportional to the voltage of the current, tends towards a limit, I , when this increases; (2) for the same salt the current limit I is proportional to

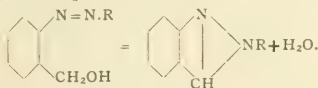
the concentration of the solution if this is very dilute (1 gm. per 1000), and varies more slowly; it tends towards a limit, J , attained more rapidly the less conducting the vapour; (3) of all the salts examined, those of potassium are more conducting than others, and their conductivity limit, I , depends on the radical acid; KI , KCl , KBr , and KNO_3 are three or four times more conducting than the other potassium salts; (4) for the same salt, A , the conductivity is only apparent if the porcelain tube is incandescent, and this increases rapidly with the temperature.

Cryoscopic Examination of Solutions in Antimony Sulphide.—MM. Guinchant and Chretien.—The authors investigate the subject of cryoscopy at very high temperatures. By the use of thermo-electric couples, the temperature of the medium can be accurately determined. The experiments were made with silver sulphide, values being obtained for the weight of this sulphide dissolved in 100 grms. of antimony sulphide, and for the lowering of the solidification-point of antimony sulphide in consequence. Experiments were also made with lead, nickel, and antimony sulphide.

Estimation of Atmospheric Formaldehyde.—H. Henriet.—The author describes the experiment by which he estimates the amount of formaldehyde in atmospheric air. The proportion he ascertains to be from 1/100,000 to 5/100,000 of the weight of the air.

Method of Identifying the Fatty Acids.—René Locquin.—M. Bouveault a short time ago described a method of identifying alcohols by preparing their pyruvic ethers and combining these with semicarbazide. Crystalline compounds are thus easily obtained. The author evolves a similar method of identifying the fatty acids. All these acids form with acetol or oxyacetone, $CH_3-CO-CH_2OH$, ketonic ethers susceptible of giving also semicarbazones, which constitute the characteristic derivatives of the acids to which they correspond. He proves that the semicarbazones thus obtained easily crystallise, are easy to purify, and have very defined fusing-points.

Transformation of Azoic Compounds with Ortho-substituted Alcohol Function into Indazolic Derivatives.—P. Freundler.—The author showed that benzene- α - α -benzyl alcohol yields phenylindazole when it is distilled or heated at 100° with dilute sulphuric acid. This reaction is absolutely general, and is effected each time that the azoic group is situated in the ortho-position with respect to a CH_2OH function:—



Limit of the Union of Diazobenzene and Phenol.—Leo Vignon.—By the direct action of one molecule of diazobenzene chloride on one molecule of phenol the author obtains paraoxyazobenzene. Two molecules of diazobenzene chloride acting on one molecule of phenol give an almost theoretical yield of phenolbisdiazobenzene. The formation of this latter body represents the limit of the union. In no case has phenoltridiazobenzene been obtained.

MISCELLANEOUS.

Action of Peroxide of Nitrogen on the Isonitrosomalonic Ethers.—L. Bouveault and A. Wahl.—If peroxide of nitrogen in excess is made to act on 50 grms. of isonitrosomalonic acid ethyl cooled in ice, at first the peroxide is dissolved, with the production of a brownish green colouration. In a short time bubbles of gas are formed throughout the mass. The temperature must be kept down, and after an hour or two the reaction is complete

and the liquid is decolorised. The product is then submitted to fractional distillation *in vacuo*, and two principal fractions are obtained; one boiling at $95-110^\circ$ under 12 to 15 m.m., the other at $110-130^\circ$. The aqueous solution of the first one gives crystals of hydrate of mesoxalate of ethyl. The second fraction is treated with ammoniacal water, and the yellow solution shaken up with ether, decanted, and decomposed with a dilute acid. The precipitated oil is purified and dissolved in absolute alcohol, and an excess of ammoniacal alcohol added. After some time a salt is deposited; this is re-crystallised in alcohol, when yellow flakes are formed, consisting of the ammoniacal salt of the nitromalonate of ethyl.—*Bull. Soc. Chim., Series 3, XXIX., Nos. 18-19.*

Production of Pure Iodine, and the Preparation of Titrated Solutions of Iodine and Sodid Hyposulphite.—L. de Koninck.—The author reviews the different known methods for procuring pure iodine for the preparation of titrated solutions. He recommends the action, by the dry way, of bichromate of potassium on iodide of potassium, feeling assured that the impurities usually contained in these two salts are generally without influence on the final product; further, it is very easy to purify these salts. The iodine is prepared by this method, by heating a very intimate mixture of one part of iodide with three-fourths of bichromate. By collecting the iodine in a tared matras or glass bulb, it is possible to prepare a titrated solution directly and rapidly.—*Bull. Assoc. Belge Chim., vol. xvii., p. 15.*

Electrolytic Estimation of Thallium (Anodic Precipitation of the Oxide).—E. Haberg.—Excellent results can be obtained by electrolysis a sulphuric solution of thallium; 0.2 to 1 gm. of the sulphate are dissolved in a platinum crucible in 80 to 100 c.c. of water; add 2 to 6 c.c. of normal sulphuric acid and 5 to 10 c.c. of acetone, electrolyse with a current varying from 1.7 to 0.3 volts at the end of the operation. The platinum crucible serves as the anode; the cathode is formed of a disc of platinum. The intensity of the current should not be more than 0.02 to 0.05 amperes at the outside; the temperature should be maintained between 50 and 55° ; the volume of the liquid should remain constant. The precipitated oxide is washed in water, twice with alcohol, once with ether, and dried for twenty minutes at $160-165^\circ$. The addition of an alkaline sulphate facilitates the electrolysis by increasing the conductivity of the solution, but in this case we must carefully wash the precipitated oxide or else we should obtain too high a figure.—*Zeit. Anorg. Chem., vol. xxxv., p. 347.*

A New Method for the Estimation of Selenium.—A. Gutbier and E. Rohn.—The authors have applied to the estimation of selenium, the method mentioned by one of them for the estimation of tellurium (*Zeit. Anorg. Chem., vol. xxxii., p. 295*). The selenium should be in the form of selenious acid, for, contrary to what has been observed with tellurium, the aqueous solutions of selenic acid are only slowly and incompletely reduced by hypophosphorous acid. In the presence of concentrated hydrochloric acid we obtain only a small quantity on selenium dissolved in the colloidal state, without any precipitate being observed. The aqueous solutions of selenious acid are precipitated slowly in the cold, and rapidly when heated. The selenium obtained is quite comparable with the tellurium produced under the same conditions. By prolonging the heating the reduction goes as far as seleniuretted hydrogen. For the quantitative determination of selenium the operations should be carried out in alkaline solution. Instead of 71.19 of selenium the authors found 71.22, 70.99, 71.08, and 71.25.—*Zeit. Anorg. Chem., vol. xxxiv., p. 448.*

The Estimation of Iron in the presence of Zirconium, by Rivot's Method.—K. Daniel and H. Leberle.—Rivot's method for the separation of two oxides of which one only is reducible by hydrogen, does not apply to the separation of oxide of iron and zirconium. The reduction of the iron only takes place in anything like a complete

manner in the presence of a very small quantity of ZrO_2 . With 1 equivalent of Zr for 50 of iron, the figure found for the iron is 0.1822 instead of 0.1830. The error increases rapidly with the percentage of zirconium. In a mixture of equal parts of iron and zirconium, the authors found 0.0882 of iron instead of 0.0933. In the experiments of Gutbier and Hüller, who recently described this method (*Zeit. Anorg. Chem.*, vol. xxiii., p. 92), and appeared to have arrived at very concordant results, the figures found are a consequence of the incomplete drying of the oxides employed. The authors have, in fact, made certain that the oxides of iron and of zirconium dried at 105° , as in these last-named chemists' experiments, retain notable quantities of water. The loss of weight observed results, therefore, from (1) the actual reduction of a portion of Fe_2O_3 , and (2), from the dehydration of the hydrated oxides ($Fe_2O_3 \cdot xH_2O$).—*Zeit. Anorg. Chem.*, vol. xxxiv., p. 393.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Vacuum Drying Machinery.—If Messrs. Ellhott will apply to Lennox and Co., Sanctuary House, Tophill Street, Westminster, they can get all details.—A. LEIBMANN, Manchester.

E. GEORGE & SONS, BOOKSELLERS.

161, WHITECHAPEL ROAD, LONDON, E.

ARE OPEN TO PURCHASE Complete Sets or short runs of the following:—*Chemical News, The Analyst Journal of the Chemical Society, 1848 to 1870, Journal of the Society of Chemical Industry, or the Publications of any other English or Foreign Learned and Scientific Societies.*—Libraries Purchased.

Current Catalogue of General Literature sent on application.

MICA.

Telephone
No. 2248
Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., & London.
MICA MERCHANTS.

Manufacturers of Mica Goods or Electrical and ALL purposes.
Contractors to His Majesty's Government.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGDON ST., E.C.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.
LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.

BOROUGH OF SWANSEA TECHNICAL COLLEGE.

LECTURER IN METALLURGY.

Applications are invited for the above Lectureship. Salary £200 per annum, rising by annual increments of £10 to £250.

The Lecturer will be expected to enter upon his duties in September. Applications, with one set of copies of testimonials, should reach the undersigned not later than THURSDAY, JUNE 30th.

Further particulars can be obtained from the SECRETARY at the College.

J. TREVOR OWEN, M.A., Principal.

UNIVERSITY COLLEGE of WALES, ABERYSTWYTH.

ASSISTANT LECTURER AND DEMONSTRATOR IN
CHEMISTRY.

The Council invite applications for the Post of ASSISTANT LECTURER and SENIOR DEMONSTRATOR in CHEMISTRY.

Applications, with copies of testimonials, should reach the undersigned, from whom further particulars may be obtained, not later than SATURDAY, JULY 9, 1904.

T. MORTIMER GREEN, Registrar.

June, 1904

UNIVERSITY OF BIRMINGHAM.

The Council invites applications for the following Appointments:—

ASSISTANT LECTURER in MATHEMATICS.

ASSISTANT LECTURER and DEMONSTRATOR in PHYSICS.

ASSISTANT LECTURER and DEMONSTRATOR in CHEMISTRY.

The stipend in each case will be £150 per annum.

The Candidates selected will be required to enter on their duties on October 3rd next.

Further particulars may be obtained from the undersigned, to whom Applications, accompanied by six copies of testimonials, should be sent not later than AUGUST 1st, 1904.

GEO. H. MORLEY, Secretary.

EDINBURGH AND EAST OF SCOTLAND COLLEGE OF AGRICULTURE.

AGRICULTURAL CHEMISTRY.

The Governors of the College will proceed at an early date to the Appointment of a Lecturer on the above subject.—Applications, accompanied by 45 copies of testimonials, should be addressed, not later than JULY 30th, to the SECRETARY, 13, George Square, Edinburgh, from whom further particulars may be obtained.

OLD PLATINUM

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver Refiners, 80, 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and Purchased.



THE CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 10 words to line)	0	3	6
Each additional line	0	0	6
Whole column	1	15	0
Whole page	3	0	0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGDON ST.,
LONDON, E.C.

INDEX.

- ABNEY, Sir W. de W.**, calculation of colours for colour sensitometers, and the illumination of three-colour photographic transparencies by spectrum colours, 212
- Accumulator, electric**, 227
- Accumulators, electric**, regulations for manufacture, 35
- Acetaldehyde solution**, action of hydrogen sulphide on, 266
- Acetals**, nitrobenzene, reaction, 119
of polyatomic alcohols of the sugar series, 235
- Acetates of the alkaline earths**, 34
- Acetol**, methylic ether of, 251
- Acetone hydrates**, 244
- Acetylene gas**, application to heating of germination stoves, 215
- Acetylglutamic acid**, 287
- Acid, abietic**, constitution, 259
- allantoic**, 143
- benzoic**, organo-metallic compounds of, 83
- bromosuccinic acid**, action on the pyridic and quinolic bases, 34
- bismutoballic**, constitution, 23
- boric**, 262
and strong acids, estimation, 60
- bromosuccinic acid**, action on the pyridic and quinolic bases, 34
- n*-campholenic racemic**, derivatives, 191
- n*-camphorylglutic**, derivatives, 191
- carbinic**, action on solutions of sodium nitrite, 191
- chaulmoigric**, constitution, 295
- chloric**, action of copper on, 269
- electrolysis of**, 106
- chloromorphosphonic acid**, *d*-, and *l*-, and *l*-methylhydrazine, isomeric salts of, 19
- crotonic**, separation of *β*- from *α*-, 140
- αβ*-dihydroxybutyric**, resolution into its optically active constituents, 99
- dilute**, apparent diminution of energy of in presence of a neutral salt of this acid, 250
- ethylthiocamphoric**, 162
- gallic**, action of hydrated oxide of osmium on acid isomers of, 227
- hydrochloric**, influence on oxidation of sulphurous acid, 238
- hydrochloric**, and oxygen, action of a mixture of on metals, 33
- hydrocyanic**, action on ammonium aldehyde and analogous combinations, 22
- hydroxyacetic**, 294
- hypophosphorous**, preparation and properties, 297
- isopropylonic**, ethers of, 22
- ketonoxanthoxybenzoic**, 141
- l*-mandelic**, esterification by menthol and boreol, 116
- methylsuccinic acid**, ester of, 177
- molybdic**, colour reactions of, 106
- n*-nitrobenzoylactic**, 70
- oxalic**, and potassium permanganate, speed of reaction between, 69
- peroxylamnesulphonic**, 13
- phosphoric**, determination, 73, 89, 101
- esterification by glycerin**, 34
- salicylic**, organo mercuric compounds of, 120
- Acid, silicic**, 251, 263
- and a alkaline and alkaline-earthly silicates**, 23
- sulphurous**, influence of hydrochloric acid on oxidation, 238
- trimethylbutyric**, 7, 7, 7, 226
- triethylglutamic**, *cis*- and *trans*-modifications of, 55
- vanadic**, and ethenol, colour reactions of, 82
- Acids, acetylenic**, 226
- decomposition by the alkalis**, 226
- hydration**, 226
- β*-ketoic**, diortho-substituted, 19
- caprylic**, and pelargonic, synthesis, 226
- crotonic**, *γ*-substituted, 262
- αα*-dimethylglutamic and *αα*-dimethylglutadic**, synthesis of, 163
- fatty**, identifying, 311
- solubility of salts of lower**, 193
- ferro-** and **ferri-hydrocyanic**, chemical equilibrium between, 169
- hydroxycarboxylic**, action of heat on, 31, 294
- β*-ketoic** and ***β*-aldehydic**, optically active esters of, 21
- manganous** and **tungstic**, complex double salt of, 288
- methodic degradation**, 191
- methylglutadic**, *β*-, *α*-substituted, 167
- metacinnamic**, *β*-, isomeric, 251
- monocetylphosphoric**, silver and lead salts of, 203
- nitrobenzoic**, reduction, 119
- oxaloyl-ethylenic**, 119
- pelargonic** and **caprylic**, synthesis, 226
- resin**, of conifer, 259
- strong**, and **boric acid**, estimation, 60
- Acid, *α*-, W.**, action of radium rays on halides of the alkali metals, 246
- principal cause of saltiness of the Dead Sea**, 13
- Acridine series**, 70
- Acylammonoketones**, isomeric change of diacylanilides into, 117, 176
- Acyl thiocyanates**, tautomeric character of, 62
- Æther***, absence of effects of motion through in relation to constitution of matter, 284
- "Africa, South, Proceedings of Chemical and Metallurgical Society of" (review)**, 46
- Africa, South, Chemical, Metallurgical, and Mining Society of**, 71
- "Agricultural Work in the Botanic Gardens and the Government Laboratory at British Guiana, Report" (review)**, 274
- Air**, formic aldehyde in, 23, 120
- Alcohol, campholenic**, and campholenic derivatives, 119
- hydrates**, ethylic, 22
- methyl**, 244
- isopropyl**, conversion into isopropyl ether, 260
- methyl**, estimation in presence of ethyl alcohol, 18
- methyl**, electric osmosis in, 237, 260
- primary phenylethyl**, 295
- trichlorisopropyl**, 166
- Alcohols, acid, nitric ethers of**, 35, 59, 227
- Alcohols, amino**, of tertiary alcoholic function, 203
- boiling-points**, 265
- condensation of acetylenic ethers with**, 197
- hexamethylenic**, mononitrobenzaldehydes, combination, 23
- hydro-aromatic**, preparation, 59
- polyatomic of sugar series**, acetals of, 238
- primary**, preparation by means of the corresponding amides, 94
- secondary**, and tertiary of fatty series, differentiation, 287
- purification and identification**, 251
- tertiary**, application of Grignard's reaction to the halogen ethers of, 275
- synthesis**, 95
- Alcoyl and alcoylenic derivatives of cyclic ketones**, preparation, 296
- Alcoyl-alkyl ketones**, 119
- Alcoyl menthones**, preparation, 286
- Aldehyde, formic**, in air, 23, 120
- β*-oxy-*n*-naphtholic**, derivatives and products of condensation, 287
- Aldehydes, aromatic**, synthesis, 83
- boiling-points**, 265
- condensation with menthyl acetate**, 21
- fatty**, synthesis, 226
- preparation**, 191
- reaction for**, 131, 251
- synthesis**, 83, 191
- transformation of primary *n*-glycols into the corresponding**, 59
- Alkali earth metals, periodides of**, 273
- metals**, action of radium rays on halides of, 246
- Alkaline and alkaline-earthly chlorates**, electrolysis with copper anode, 293
- carbonates**, behaviour of phenolphthalein in presence of, 27
- dissociation**, 59
- chlorides**, electrolysis of resistance of iridio-platinum anodes used in, 138
- earth manganese-manganates**, 155
- metals**, fluorochlorides, fluorobromides, and fluoiodides of, 106
- periodides of**, 273
- carbis**, acetates of, 34
- hydroxides and ammonia**, relative strengths of as measured by their action on cotanamine, 17
- metals**, flame spectra of, 130
- metopurassia**, estimation, 114
- Alkaloids**, precipitation by nitrate of uranium, 26
- Alkyl iodides**, chemical dynamics of, 140
- alkylsilicon chlorides**, preparation, 81
- Alkyl ureas**, decomposition, 273
- Allantoin**, 143
- Allen, E. T.**, precipitation and separation by weak organic bases, 43, 63, 76, 88, 103
- Alkyl ketones**, 179
- Aloy, J.**, precipitation of some alkalooids by uranium nitrate, 26
- Alumina and iron**, separation, 63
- precipitation by phenylhydrazine**, 44
- Aluminium and iron**, separation, 44, 15
- chloride**, compounds with organic substances containing oxygen, 294
- lead alloys**, 261
- tin alloys**, property of, 286
- welding**, 117
- zinc alloys**, 274
- "American Electro-chemical Society, Transactions" (review)**, 16, 129
- American Electro-chemical Society**, 156
- Amidon**, retrogradation and coagulation, 71
- retrograde**, formation and saccharification of, 101
- starch**, retrogradation of, 59
- Amines, aromatic**, action of chloroacetamide on, 293
- cyclic**, 261
- primary**, at boiling-point, action of PCl_5 on, 298
- di-alcoholic aromatic**, union of cinchophenyl salts with, 168
- primary and tertiary**, iodides of mercur-ammonium of, 34
- synthesis of cyclohexylamine and two other**, 155
- Aminoketones**, aromatic, intramolecular re-arrangement in derivatives of, 117
- Aminonitriles**, 59
- Ammeter**, hot-wire, for measuring very small alternating currents, 178
- Ammonia, alcoholic**, action of calcium on, 263
- and alkaline hydroxides**, relative strengths of as measured by their action on cotanamine, 17
- nitrate of silver compounds**, 275
- liquid**, osmosis in, 59
- Ammonium aldehyde**, action of ammonia on, 22
- metals**, action of carbonic anhydride on, 179
- thiocyanate**, 141
- "Analysis and Assaying, Metallurgical" (review)**, 166
- Analytical operations**, use of organo-magnesian compounds in, 139
- Anhydride, carbonic**, action on ammonium salts, 179
- Anilines, aqueous solutions of**, action of carbon dioxide on in presence of nitrites, 59
- attempt to make take the form of amino-nagenation phosphate**, 35
- homologues**, hydrogenation, 310
- hydrochloride**, hydrolysis, 77
- hydrogenation**, 155
- Anilines, derivatives of highly substituted**, 81
- "Annuaire pour l'An 1904" (review)**, 22
- Anode**, influence of the physical nature of on constitution of electrolytic peroxide of lead, 278
- Anodes**, iridio-platinum, used in electrolysis of alkaline chlorides, resistance of, 138
- Anthracene oxidation**, electrolytic, 236
- Anthraquinone**, action of phenylmagnesium bromide on, 130
- Antimony**, 173
- and antimony trisulphide**, mixture, 119
- and tellurium**, separation, 168
- estimation**, 299

- Antimony sulphide and bismuth proto-sulphide, fusibility of mixtures of, 12
solutions in, cryoscopic examination, 311
trisulphide and antimony, mixtures, 119
- Apparatus for measuring contents of human blood, 245
for electrical study of stationary electric waves on spiral wires, 245
for regulating the action of vacuum pumps, 191
volumetric, accurate, 240
- Archibald, E. H., revision of the atomic weight of rubidium, 22
- and D. McIntosh, basic properties of oxygen, 295
and J. W. Walker, ionisation and chemical combination in the liquefied halogen hydrides and hydrogen sulphide, 294
- Argon in gases of hot springs of Guelouise, 250
- Aromatic compounds obtained from the hydro-aromatic series, 93
- Arseniate, methyl-amino-magnesian, 33
triethylamino-magnesian, 35
- Arsenites, amino-magnesian, 35
- Arsenic and copper alloys, 200
estimation, electrolytic, 272
in all the organs of the animal economy, 208
in bird's eggs, 262
in organic matters, detection, 226
in organism, Berthelot's calorimetric bomb to prove, 291
medicinal, elimination and distribution of in the organism in the form of methyl arsenate of soda, 23
sesquioxide, constitution, 30
sulphide, colloidal solutions of, precipitation, 215
systematic alloying of, 12
yellow, 71
- Ascoli, M., electric osmosis in liquid ammonia, 59
- Ash in the human body, 72
report on, 41, 54
- "Assaying and Analysis, Metallurgical" (review), 165
- Atomic weight, relation of specific heat to, 165
weights, international, 305
of oxygen and hydrogen, 261
report of International Committee, 68, 164, 173
- Atoms, valence of, and negative electricity, connection between, 25
- Attwell, H. M., and M. O. Forster, borylcarbidide, 235
- Atwater, W. O., and F. G. Benedict, "Experiments on the Metabolism of Matter and Energy in the Human Body" (review), 261
- Auger, V., systematic alloying of arsenic, 12
and M. Billy, alkaline earth manganate-manganates, 155
Australian patent law, 167
- Auxetophone, 245
- Ayrton, Mrs. H., origin and growth of ripple marks, 308
- Azoic compounds, 22
with ortho-substituted alcohol functions, transformation into indazolic derivatives, 311
- BACTERIA**, radio-activity of, 245
- Bacteriology, King's College, London, 12
- Bacterium, oxidising, 287
- Bagley, G., and T. H. Easterfield, resin acids of conifer, 259
- Balance, magnetic, 308
- Balances, chemical, new design for, 167
- Balch, D. M., catalogues gratis, 167
- "Baltimore Lectures" (review), 213
- Bamber, M. K., estimation of the adulterant in citronella oil, 21
- Barger, G., microscopic method of determining molecular weights, 59
- Barium, amide and nitride of, 34
ammonium, action of gases on, 13
and magnesium, sodium, calcium, and strontium peroxides, iodometry of, 96
and radium, separation, 97
law of thermic constants, and heat of formation of compounds of, 123
poly-meta-iodanthate, 198
- Barkla, C. G., energy of secondary X-ray radiation, 178
- Barrel, E., chlorination of phenyl carbonate in presence of antimony chloride, 251
in presence of iodine, 238
- Baskerville, C., elements, verified and unverified, 109, 121, 135, 150, 162, 179, 186, 194, 210
and G. F. Caillet, contributions to the chemistry of the rare earths, 107
and J. H. Holland, contributions to the chemistry of the rare earths, 184
and G. F. Kunz, action of radium rays and ultra-violet light on minerals, 145
and E. G. Mott, contributions to the chemistry of the rare earths, 172
and R. Stevenson contributions to the chemistry of the rare earths, 153
and J. W. Turrettine, contributions to the chemistry of the rare earths, 147
- Bastian mercury-vapour lamp, 126
- Beauchamp, H., and G. Chavanne, new method of estimation of halogen elements in organic bodies, 82
and F. Rivals, separation of iodine from alkaline halogen salts of iodine, chlorine, and bromine, 12
- Baudouin, A., electric osmosis in methylic alcohol, 237, 286
- Bauge, G., crystalline chromous tartrate, 297
- Bayley, T. (obituary), 310
- Beck, Mr., microscopes, 94
- Bequerrel, H., "Recherches sur l'activité de la Nouvelle de la Matière" (review), 155
- Béhal, A., isomer of borneol, 119
and M. Sommelet, method of synthesis of aldehydes, 83
- Beilby, G., and J. H. and S. states in metal, 307
- Beis, C., action of mixed organo-magnesium compounds on phthalimide and phenylphthalimide, 244
- Bellamy, A. E., and R. S. Morrell, separation of β -crotonic acid from a crotonic acid, 140
- Benedict, F. G., and W. O. Atwater, "Experiments on the Metabolism of Matter and Energy in the Human Body" (review), 261
- Bennett, W., notes on non-homocentric pencils and the shadows produced by them, 57, 153
- Benzene in illuminating gas, determination, 14, 29
in poisoning by coal-gas, 74
- Benzenebenzochloride, action of sodium methoxide on, 272
- Benzoylaminoethylbenzophenones, transformation of dibenzoylulimides into isomeric, 176
- Benzylidene aniline, additive products with ethyl acetate and ethyl methylacetate, 259
chloride, action of sodium methoxide on, 272
- Berg, A., influence of hydriodic acid on oxidation of sulphurous acid, 238
- Berghelli, C., fermentation of the indigo plant, 296
- Berthelot, M., use of alternating currents in chemistry, 286
Berthelot's calorimetric bomb to prove existence of arsenic in organism, 291
- Bertrand, G., existence of arsenic in bird's eggs, 262
oxidation of gaycol by laccase, 59
pressure regulator for fractional distillation, 237
separator for fractional distillation, 239
use of Berthelot's calorimetric bomb to prove existence of arsenic in organism, 291
- Beryllium and thorium, separation, 77
and titanium, separation, 76
and zirconium, separation, 77
- Beulaygue, E., sodium monosulphide as an indicator in the estimation of glucose by Fehling solution, 71
- Bevan, E. J., and C. F. Cross, hydrosulphides, 155
- Beveridge, P. J., liquid state, 169, 181
theory of electrolytic dissociation, 82
- Billy, J., and V. Auger, alkaline earth manganate-manganates, 155
- Bird's eggs, arsenic in, 262
- Bismuth, 174
and tannin compounds, 238
estimation, 10
in the form of chromate, iodometric estimation, 143
arseniate, 87
use as a means of separation in rare earth series, 25
oxide, hydrated, action on acid isomers of gallic acid, 227
phosphate, 87
proto-sulphide and antimony sulphide, fusibility of mixtures of, 12
proto-sulphide and silver sulphide, fusibility of mixtures, 12
salts, crystallised, production, 87
sub-nitrate, 87
- Blaise, E. E., alcoyl-allyl-ketones, 119
allyl and propenyl -alcoyl ketones, 179, 275
method of preparation of aldehydes, and methodic degradation of acids, 191
- Blanc, G., synthesis of α -dimethylglutaric and α -dimethylsuccinic acids, 168
and M. Desfontaines, certain derivatives of α -campholitic acid and α -campholenic carboxylic acid, 101
and A. Hallier, new syntheses effected by means of molecules containing the methylene group associated with one or two negative radicals, 59
- "Bleaching, Electrical, and Hypochlorite" (review), 46
- Block, E., "Alfred Werner's Theorie des Kohlenstoffatoms und die Stereochemie der Kohlenstoffischen Verbindungen" (review), 45
- Blondlot rays, application to chemistry, 234
emitted during chemical reactions, origin, 274
- Blood, human, apparatus for measuring contents of, 245
influence of chemical form under which an element is presented to the organism on rapidity of its passage into, 24
- Boardman, T. H., and W. French, "Practical Chemistry" (review), 214
- Bodlander, G., and O. Storbeck, contribution to the study of cuprous compounds, 59
- Bodroux, F., general method of synthesis of aldehydes, 191
synthesis of aromatic aldehydes, 13
- Body, human, ash in, 72
- Bodtler, E., formation of chloro-anilines, 287
- Boiling-points of homologous compounds, 265
- Bolduan, C., and A. Wassermann, "Immune Sera" (review), 310
- Bomb, calorimetric, to prove existence of arsenic in organism, 291
- Bone, W. A., and J. Drugman, action of ozone on, 250, 273
and W. E. Stockings, slow combustion of ethane, 246
J. J. Sudborough, and C. H. G. Sprankling, acid esters of glycolic acid, 291
- Bonnicksen, B., new dilatometer, 127
- Boone, W. T., "Safe! Course in Experimental Chemistry" (review), 267
- Boote well-water, composition, 9
- Borneol, isomer of, 119
- Bornylcarbidide, 235
- Bottone, S., "Radium and All About It" (review), 250
- Boucher, C., new method for attack of galenas and chalcopyrites, 56
- Bouchonnet, A., and C. Chabrie, preparation of iridium sesquioxide, 34
- Boudouard, O., allotropic transformations of nickel steels, 130
new method of determining critical-points of iron and steels, 34
- Boulough, R., formation of phosphorus sulphides in the cold, 130
- Bourin, F., and C. Matignon, general method of preparation of anhydrous chlorides, 179
transformation of oxides and oxygen salts into chlorides, 293
- Bousfield, E. G. P., experiments with a new primary cell, 201
note on determining accurately the percentage of ozone in gases not dissociated by moderate heat, 201
- W. R., purification of water by continuous fractional distillation, 141
- Bouveault, L., application of Grignard's reaction to halogen ethers of tertiary alcohols, 275
- Jecker Prize, 58
- Bouvenot, L., identification of alcohols, 251
- and G. Blanc, preparation of primary alcohols by means of corresponding amides, 94
- and A. Wahi, action of peroxide of nitrogen on isonitrosomalonic esters, 311
granular synthesis of the fatty aldehydes, 226
nitro-isobutylene, 31
preparation of diketonic esters, 298
reduction of ω -nitrostyrene, 23
- Brathwaite, J. O., "Year-book of Pharmacy" (review), 21
- Braun, G., and A., "Dictionnaire de Chimie Photographique" (review), 274
- Bread, examination of ancient samples, 109
- Brenans, P., new tri-iodine phenol, 34
- Briggs, S. H. C., ammoniacal double chromates and molybdates, 235

- Briggs, S. H. C., hexahydrated double chromates, 235
- Brisson, M., some amino-magnesian arsenates, 35
- and C. P. Porter, attempts to make aniline and urea take the form of amino-magnesian phosphate, 35
- some amino-magnesian phosphates, 34
- "British Guiana, General Information with regard to the Gold, Diamond, and Forest Industries" (review), 130
- "British Guiana, Report on Agricultural Work in Botanic Gardens and Government Laboratory at" (review), 124
- "British Patents for Inventions, Grant and Validity of" (review), 124
- Brochet, A., action of copper on chloric acid, 269
- basic copper chloride, 293
- electrolysis of alkaline and alkaline-earth chlorides with a copper anode, 293
- of chloric acid and chlorates, 106
- electrolytic solution of platinum, 274
- formation of basic salts of copper under influence of electrolysis, 279
- and J. Petit, influence of complex ions in electrolysis by alternating currents, 143
- use of alternating currents for electrolysis, 130
- Bromates, estimation, 95
- Bromine, action on 1:5-dichloro-1:1-dimethyl- Δ -2:4-dihydrobenzene, 95
- alkaline halogen salts, separation of iodine from, 12
- Bromphenol, action of magnesium and organo-magnesium compounds on, 262
- Brown, J. C., potable waters in South-West Lancashire, 6
- Brownlow, H. W., volumetric method for the estimation of mercury fulminate, 303
- Brunk, A., estimation of ozone, 243
- Brusil, L., preparation of hydro-aromatic alcohols, 52
- Brushite, artificial production, 203
- Buffalo cow, sugar in milk of, 262
- Buller, L. M., obtaining calcium carbide, 238
- Bunel, L. J., and C. Marie, estimation of persulphates, 113
- Burgess, C. H., and D. L. Chapman, nature of a solution of iodine in aqueous potassium iodide, 176
- photochemically active chlorine, 152
- H. K., and T. H. Page, composition of distilled oil of times and a new sesquiterpene, 176
- Burke, Miss K. B., and F. G. Donnan, chemical dynamics of the alkyl iodides, 145
- Burns, G., organo-mercuric compounds of salicylic acid, 120
- Butter-fat analysis, interdependence of the physical and chemical criteria in, 80
- CADMIUM** arsenide, 167
- salts, 71
- solubility estimation, 114
- silver series of alloys, properties of, 86
- Cano, J. C., halogen derivatives of diphenyl and dihydroxydiphenyl, 18
- phenyl, 18
- Calcium, action on alcoholic ammonia, 263
- strontium, barium, magnesium, and sodium peroxides, iodometry of, 96
- acetate, ignition of material with, 55
- Calcium carbide, obtaining, 238
- preparation, 191
- chloride, electrolysis, 297
- oxalate, precipitation of magnesium oxalate by, 146
- "Calculating Tables" (review), 214
- "Calendar, Imperial University of Tokyo" (review), 240
- Californian lauric constituents of essential oil of, 224
- Callender, H. L., projection of indicator diagrams of a petrol motor, 306
- Cambridge Scientific Instrument Company, bibliography, 245
- Camphor, ethylidene, 168
- hydraminates, 19
- Campholene derivatives, 119
- Camphor, ethylidene, 168
- monopoly in Japan, 250
- Capacities, measurement of small inductances and, 177
- Caprolyl thiocarbamide, 273
- Carbide, catalytic activity, 119
- Carbimides, optically active, 259
- "Carbon Atom, A. Fred Werner's Theory of the, and the Stereochemistry of the Carbo-cyclic Compounds" (review), 46
- Carbon, action on quicklime at the temperature of fusing platinum, 119
- atomic weight, 297
- combination of aqueous solutions of aniline in presence of nitrates, 59
- on solutions of sodium nitrite, 130, 155
- dilphide solution, action of heat and light on mixtures of phosphorus sesquisulphide and sulphur in, 130
- monosulphide, gaseous, 25
- monoxide and oxygen, composition, 114
- sulphide, constants of, 83
- Carnot, A., "Traité d'Analyse des Substances Minérales" (review), 155
- Caro, P., and F. Fonze, Diacon, M.M., toxicity of nitroprussiate of soda, 226
- volumetric estimation of alkaline nitroprussates and of soluble salts of cadmium, 114
- Carré, P., etherification of phosphoric acid by glycerin, 34
- phosphoric ethers of glycerin, 50
- of glycol, 139
- Cartaud, G., and F. Osmond, meteoric iron, 34
- Caspian Sea, analysis of the combustible gas given off in the, 78
- Catalogues gratis, 167
- Cattell, G. F., and C. Baskerville, contributions to the chemistry of the rare earths, 197
- Cavender, J., silver and lead salts of monocalciphosphoric acids, 203
- Cell, primary, experiments with, 201
- "Ceramic Calculations, Text-book of" (review), 274
- Cerium, 174
- and phenylhydrazine, 64
- behaviour toward organic bases, 15, 27
- Ceric earths, fractionation, 277
- Chabrie, C., and A. Bouchonnet, preparation of iridium sesquiseleide, 34
- Chalcopyrites, attack of, 56
- Charges, intramolecular and originally reversible, extending over prolonged periods, 115, 196, 207
- Chapman, D. L., and C. H. Burgess, nature of a solution of iodine in aqueous potassium iodide, 176
- photochemically active chlorine, 152
- Charabot, B., and A. Hebert, influence of its surroundings on vegetable acidity, 227
- Charichoff, K. V., analysis of the combustible gas given off in the Caspian Sea, 78
- Chassagnat, A., preparation and properties of pure colloidal silver, 218
- Chattaway, F. D., dibenzoylchlorimide, 93
- intramolecular rearrangement in derivatives of aromatic aminoketones, 117
- isomeric change of diacyl-anilides into acylamino-ketones, 117
- and W. H. Lewis, isomeric change of diacylanilides into acylaminoketones, 176
- and J. M. Wadmore, derivatives of highly substituted anilines, 81
- Chaumoooga seeds, constituents, 294
- Chavanne, G., ethers of isopropylmucic acid, 22
- and H. Baubigny, estimation of halogen elements in organic bodies, 82
- Chelsea, South-Western Polytechnic, 24, 227
- "Chemical and Metallurgical Society of South Africa, Proceedings" (review), 46
- Chemical balances, new design for, 11
- combination and ionisation, 234
- Metallurgical, and Mining Society of South Africa, 71
- Society, 17, 67, 80, 92, 114, 140, 152, 175, 178, 220, 235, 245, 259, 271, 293
- President's address, 190
- report of Council, 189
- Chemicals, adulterated, 180
- "Chemistry, Aids to" (review), 22
- "Chemistry, Analytical, Short Manual of" (review), 47
- "Chemistry, Descriptive" (review), 237
- "Chemistry, Elementary Practical" (review), 46
- "Chemistry, Experimental, Safe Course in" (review), 261
- "Chemistry, General, Laboratory Outline of" (review), 154
- "Chemistry, Inorganic, Elements of" (review), 166
- "Chemistry, Inorganic, Karl Heumann's Directions for Lecture Experiments in" (review), 166
- "Chemistry, Inorganic, Principles of" (review), 261
- "Chemistry, Mineral, Industries of" (review), 46
- "Chemistry, Photographic, Dictionary of" (review), 274
- "Chemistry, Physical, Introduction to" (review), 214
- "Chemistry, Physical, Introduction to the Study of" (review), 154
- "Chemistry, Physical, Journal of" (review), 167
- "Chemistry, Practical" (review), 214
- Chemistry, application of Blondlot rays to, 234
- of the rare earths, 147, 158, 172, 184, 191
- position in medical curriculum, of University of London, 65
- use of alternating currents in, 286
- what physical chemistry has done for, 90, 105
- Cheeneau, G., apparent diminution of energy of a dilute acid in presence of a neutral salt of this acid, 250
- Chloracetamide, action on aromatic amines, 298
- Chlorates, electrolysis of, 166
- estimation, 95
- Chlorides, anhydrous, preparation, 179
- detection in presence of bromides, 229
- Chlorides, transformation of oxides and oxygen salts into, 203
- Chlorine, action of light on, 250
- of silent discharge on, 152
- alkaline halogen salts, separation of iodine from, 12
- and hydrogen, union, 152, 296
- density of, 58
- determination, 55
- in plants, 55
- methods for, 56
- photochemically active, 152
- Chloroanilines, formation, 287
- Chree, C., law of action between magnets, 284
- whirling and transverse vibrations of shafts, 153
- Chrétien and Guinchant, M.M., cryoscopic examination of solutions in antimony sulphide, 311
- Chromates and molybdates, ammoniacal double, 235
- hexahydrated double, 235
- Chromium and iron, separation by fused potassium nitrate, 183
- and vanadium, separation, 182
- estimation, colorimetric, 268
- Chrysanthemum, culture, chemical study of, 60
- Cilioscrobe, 308
- Clarke, F. W., report of committee on atomic weights, 164, 173
- Clow, F., and J. B. Coleman, "Elementary Practical Chemistry" (review), 21
- "Classification of Elementary Substances" (review), 225
- Cobalt and iron, separation, 250
- Coffinger, L., solubility of hard copals, 24
- Cohen, J. B., and P. Hartley, nitration products of isomeric dichlorobenzenes, 297
- and J. Marshall, reduction of 2:6-dinitrotoluene with hydrogen sulphide, 177
- and J. Miller, influence of substitution in nucleus on rate of nitration, 180
- H. S. Raper, and J. T. Thompson, action of sodium hypochlorite on aromatic sulphonamides, 153
- Coherence and coherence, 285
- Coleman, J. B., and F. Clives, "Elementary Practical Chemistry" (review), 21
- College system and technical research, 230
- Collie, J. N., and Sir W. Ramsay, spectrum of radium emanation, 301
- Colloidal solutions, 202
- Colloids, preparation of, 202
- Colouring matter of indigo, constitution, 238
- matters, some natural, 18
- triphenylmethane, 247
- Colour, and conditions for colour sensitometers, 212
- Colson, A., acetates of alkaline earths, 34
- application of Blondlot rays to chemistry, 234
- origin of the Blondlot rays emitted during chemical reactions, 274
- Combustion, calculating heats of, 122
- heats of nitrated organic compounds, 237
- Compounds, connection between volatility of, and chemical forces at play within the molecule, 241
- homologous, boiling-points, 265
- inorganic, systematic classification, 120
- nitrated organic, heat of combustion, 237
- optically active, influence of solvents on rotation, 297
- Conduche, A., and L. J. Simon, new reaction of aldehydes, 251
- Confere, A., acids of, 152
- Constants, physical, at low temperatures, 205, 217

- Copals, hard, solubility, 24
 "Copper, Electrolytic Refining of" (review), 225
 Copper, action on chloric acid, 269
 Copper, arsenic alloys, 200
 anode, electrolysis of alkaline and alkaline-earth chlorates with, 293
 estimation, iodometric, 288
 influence on silvering of glass, 23
 chloride, basic, 293
 salts, basic, formation, 279
 Cosyns, G., and H. Wuyts, action of sulphur on organo-magnesian compounds, 227
 Cowper-Coles, S. O., welding of aluminium, 117
 Crepieux, P., and F. Reverdin, nitration of aceylalcol, 287
 Crocker, J. C., and F. H. Lowe, picryl derivatives of urethane and thiourethane, 235
 Crookes, Sir W., and J. Dewar, London water supply, 52, 85, 141, 211, 242, 304
 Cross, C. F., and E. J. Fevan, hydrocellulose, 235
 Crossley, A. W., aromatic compounds from hydroaromatic series, 93
 Cunyngame, H. H., muffle and melting furnaces, 245
 Cupel, magnesia, 304
 Cuprous compounds, 59
 Cuic and Dewar, Profs., examination of sample of gas occluded in radium bromide, 35
 Current, alternating, propagation along a telephone cable, 306
 Currents, alternating, hot-wire ammeter for measuring very small, 178
 instruments for measurement of large and small, 248
 use for electrolysis, 130
 in chemistry, 286
 "Cyanide Process of Gold Extraction" (review), 142
 "Cyaniding Gold and Silver Ore" (review), 249
 Cyanogen estimation, 229
 Cyclohexane and its chlorised derivatives, 298
 Cyclohexanol and cyclohexanone, preparation from phenol, 33
 Cyclohexylamine and two other amines, synthesis, 155

DAHMER, G., and F. W. Kuster, precipitation of colloidal solutions of sulphide of arsenic, 215
Daniel, K., and H. Leberle, estimation of iron in presence of zinciron, 311
Darling, U. R., thin-film electrolysis, 165
Davis, O. C. M., and F. E. Francis, action of nitrogen sulphide on organic substances, 93
Dawson, H., formation of peroxides in organic solvents, 152
 and Ethel Elizabeth Goodson, formation of peroxides in nitrobenzene solution, 273
D'Avenne, A., ratio between solubility of lime in presence of alkalis, and caustification of alkaline carbonates, 298
 solubility of hydrated sulphate of lime in solutions of sea-salt, 9
De Forcrand, M., zinc peroxides, 95
De Koninck, L., production of pure uric acid, 311
De la Roche, E., phenolic urethanes of piperidine, 255
De Schulten, A., production of crystallised salts of bismuth, 97
 research on dicalic phosphate, 203
De Watteville, C., flame spectra of the alkaline metals, 130
 Dead Sea, principal cause of saltness, 13
Debourdeaux, L., estimation of chlorates, bromates, and iodates, 95
 of nitrogen, 238
 titration of manganese, 83
Defacoz, E., fluochlorides, fluorobromides, and fluoiodides of the alkaline earth metals, 166
 preparation of anhydrous and crystalline fluorides, 59
Delange, R., dichloromethenoxypyrocarbonate and propyl pyroacetate carbonate, 143
 and C. Moreau, amyl chloro-arylic ethers, 226
 decomposition of acetylenic acids by alkalis, 226
 general observations in the acetylenic acids, 226
 hydration of acetylenic acids, 226
 new fatty acid, 7, 7', 7'', 7'''-methylbutyric acid, 226
Delépine, M., action of hydrocyanic acid on ammonium aldehyde and on analogous ammoniures, 22
Demarçay, E., life and work of, 137
 Design, G., reactions of pinacoin and of pinicoin, 35
Dennis, L. M., and J. G. O'Neill, determination of benzene in illuminating gas, 14, 29
Denso, P., resistance of iridium carbon anodes used in electrolysis of alkaline chlorides, 138
Dervin, E., heat and light on mixtures of phosphorus sesquisulphide and sulphur in carbon disulphide solution, 130
Descudé, M., symmetric bichloromethyl oxide, 275
Desonjoux, H., α -substituted β -methyladipic acids, 107
 and G. Blanc, derivatives of α -camphyllic acid and α -camphyllic racemic acid, 191
Dewar, J., physical constants at low temperatures, 205, 217
 and Sir W. Crookes, London water supply, 52, 85, 146, 211, 242, 304
 and C. Profs., examination of a sample of gas occluded in radium bromide, 85
 and H. O. Jones, chemical reactions of nickel carbonyl, 68
Di-sodium tetra-lanthanate, 198
Diacylanilides, isomeric change into acylanilones, 117, 176
Diagram, preparation of, 128
 "Diamond, Gold, and Forest In" (review), 130
Diazobenzenes and phenol, limit of union, 311
 action on diphenylchloride, 275
Dibenzoylchlorimide, 93
Dibenzoyltoluidines, transformation into isomeric benzoylaminomethyl-benzophenones, 126
Dichlorobenzenes, nitration products of the isomeric, 297
Dichloromethene-dioxypropylbenzene, 143
"Dictionary of Hygiene" (review), 22
"Dictionary of Photographic Chemistry" (review), 274
"Dictionary, Technological and Scientific" (review), 275, 303
Didymium orthophosphate, 299
 salts containing phosphoric acid, absorption spectra of solutions of, 299
Difraction and interference, 57
Dihydroxydiphenyl, halogen derivatives of, 18
Diketones, β -, 140
 Dilatometer, 127
Dinaphthopyranic series, 262
Dinitroethanol, 2, 6-, reduction with hydrogen sulphide, 177
Dipentene, synthesis, 233
Diphenyl, halogen derivatives of, 18
Diphenylamine, action of diazo-benzene chloride, 275
Diphenylanthracene, 310
Diphenylhydrazine, symmetric, 310
 "Directory of Paper Makers of the United Kingdom" (review), 193
 "Directory, Paper Trade" (review), 168
 "Dispensing Made Easy" (review), 142
Dissociation, electrolytic, theory of, 31, 37, 32, 202
 "Distillation, Fractional" (review), 129
Distillation, fractional, separator for, 239
 pressure regulator for, 239
Distillates, tar, accidents in, 35
Durieux, L., 130
Divers, E., constitution of nitric peroxide, 18
 peroxylaminesulphonic acid, 18
Dixon, E., 273
 organic phosphorus compounds, 116
 W. E., and O. Inchley, ciliolacrine, 308
Dobbie, J. J., A. Laucer, and C. K. Tinkler, relative strengths of alkaline hydroxides and of ammonias as measured by their action on cotinine, 17
Doby, G., action of calcium on alcoholic ammonia, 263
Documents, filing, Stolzenberg system, 269
Donnan, F. G., and Miss K. B. Burke, chemical dynamics of alkali iodides, 140
Doran, R. E., tautomeric character of the acyl thiocyanates, 92
Dreaper, W. P., technical research and the college system, 230
Drugman, J., and W. E. Stoulling, action of hydrogen sulphide on formaldehyde and acetaldehyde solutions, 260
 and W. A. Bone, action of ozone on ethane, 273
Drugs, adulterated, 180
"Drugs, Their Production, Preparation and Properties" (review), 142
Drying machine, vacuum, 312
Du Jassoneux, Binet, and H. Moisan, MM., density of chlorine, 58
Dubreuil, L., action of bromosuccinic and dibromosuccinic acid on pyridic and quinolic bases, 34
Duddell, W., some instruments for the measurement of large and small alternating currents, 248
 apparent volta-lisation of silicon in hydrogen, 286
 formation of hydrogen silicide, 261
 reduction of silicon by hydrogen, 286
Dunstan, A. E., viscosity of liquid mixtures, 260
Duval, H., nitric ethers of acid alcohols, 35, 50, 247
Dyer, B., and F. W. E. Shrive, 16
 Manuring of Market Garden crops" (review), 95

EAKLE, A. S., "Mineral Tables for the Determination of Minerals by their Physical Properties" (review), 190
 Earle, rare, series, use of bismuth as a means of separation in, 52
 Earths, alkaline, acetates of, 34
 ceric, fractionation, 277
 rare, chemistry of, 147, 158, 172, 184, 197
Easternfield, T. H., and G. Bagley, resin acids of the conifers, 259
 and O. Silberrad, studies on ethyl carboxylglutarate, 259, 296
Ebler, E., and E. Kiroevanagel, use of hydroxylamine and hydrazine in qualitative analysis, 203
Eder, J. M., and E. Valenta, invariability of the wave-lengths in the spark and arc spectrum of zinc, 98
Edwards, V., scale for chemical valuation of soils, 197
 rapid soil analysis, 183
Eggs, birds, arsenic in, 262
Ehrfeld, R., speed of the reaction between permanganate of potassium and oxalic acid, 60
Electric accumulator, 287
 accumulators, manufacture of, regulations for, 35
 furnace, 307
 distribution and spectra sparks, distribution of, 235
 waves, stationary, on spiral wires, apparatus for metrical study of, 245
 "Electricity, Subject-label of Works on, in the Library of the Patent Office" (review), 310
 Electricity, negative, and the valence of atoms, connection between, 25
 "Electro-technics, &c., Subject-label of Works on, in the Library of the Patent Office" (review), 310
 Electrolysis, applications to separation of metals from one another, 110, 113, 126
 influence of complex ions in, 143
 of alkaline chlorides, resistance of triode-platinum anodes used in, 138
 solutions, hydrates in concentrated aqueous, 157
 thin-film, 165
 use of alternating currents for, 130
 "Electrolytic Preparations" (review), 201
Electroscope, portable, 128
Element, influence of chemical form under which it is presented to organism on rapidity of its passage into the blood, 24
Elements and compounds, 220
 halogen, in organic bodies, estimation, 82
 verified and unverified, 109, 121, 135, 150, 162, 170, 186, 194
 why are some so much more abundant than others, 47, 58, 113
 "Elementary Substances, Classification" (review), 225
Elbs, K., "Electrolytic Preparations" (review), 201
Elliott and Sons, vacuum machinery, 288
Emanation substance, 267
Emanum, 267
"Energy and Matter in the Human Body, Experiments in Metabolism of" (review), 261
Engelhardt, V., "Hypochlorite und Elektrische Bleiche" (review), 45
 and F. W. Richards, "Electrolysis of Water" (review), 214
 and T. Uike, "Die Elektrolytische Raffination des Kupfers" (review), 225
Enock, F., colour photographs of living insects, 309
 "Entropy" (review), 225

- Epichlorhydrin, action on sodium acetylacrylate, 30
- Epiclaurine, constitution, 92
- Erdmann, H., constitution of sesquioxide of arsenic, 30 and V. Unsch, yellow arsenic, 71
- Esters, acid, of methylsuccinate, 127
- of β -ketonic and β -aldehydic acids, optical activity, 21
- oxamic, amino-ethers and allied compounds corresponding with, 253
- Etard, A., life and work of Eugene Demarcq, 137
- Ethane, action of ozone on, 273
- combustion, slow, 245
- Ethanol and vanadic acid, colour reactions of, 32
- Ether, chloroacetylacetic, 143
- homomaleic, 130
- isopropyl, conversion of isopropylalcohol into, 250
- methylene, action of, 251
- oxides, halogen, 251
- preparation by means of magnesium compounds and halogen methylic esters, 215
- Ethers, acetylenic, condensation with alcohols, 107
- amylchloroacrylic, 226
- and olein, biochemical synthesis, 130
- diketonic, preparation, 298
- halogen, of tertiary alcohols, application of Grignard's reaction to, 275
- isotrisomaleic, action of peroxide of nitrogen on, 311
- nitric, of acid alcohols, 35, 59, 227
- of isopropionic acid, 22
- phosphoric, of glycerin, 70
- of glyco, 130
- Ethyl acetacetate, additive products of benzylidene aniline with, 259
- bro-nitrocarboxylate, action of ethyl bro-nitrocarboxylate, 296
- glutarate, 296
- carboxylate, formation, 246
- carboxylate, 259, 296
- β -isopropionic, action on ethyl diisododecanetetracarboxylate, 176
- methylacetacetate, additive products of benzylidene aniline with, 259
- iodi-carboxylate, action of ethyl bromo-carboxylate on, 296
- of halogens on, 259
- of chlorides, rotating values at different temperatures, 259
- Ethynidene camphor, 168
- Eurpium, 179
- Everett, J. D., normal piling as a consequence with Osborn & Reynolds's theory of universe, 212
- "Extra Pharmacopoeia" (review), 399
- FARADAY** lecture, 220
- Society, 117, 165, 200, 236, 307
- Fat, butter, analysis, interdependence of physical and chemical properties in, 80
- Fats, thermostat for use in connection with the refractometric examination of, 80
- Fatty acids, hydrogen derivatives of, action of reduced nickel on in presence of hydrogen, 143
- Fawcett, C. R., decomposition of alkylates, 273
- relation between chemical composition of organic substances and density of their solutions, 117
- studies in viscosity, 236
- Fermentation in the indigo plant, 206
- Ferribach, A. L. Maquenne, and J. Wolff, resorption and coagulation of amideon, 71
- Filing documents, Stenograph system, 259
- Findlay, A., freezing-point curves of dynamic isomerides, 141
- "Phase Rule and its Applications" (review), 201
- "Fire and Explosion Risks" (review), 286
- Fleming, J. A., apparatus for electrical study of stationary electric waves on spiral wires, 245
- hot-wire ammeter for measuring very small alternating current, 248
- measurement of small inductances and capacities, 177
- model illustrating the propagation of an alternating current along a telephonical, 306
- Fluobromides, fluochlorides, and fluoiodides of alkaline-earth metals, 106
- Fluorides, anhydrous and crystalline, preparation, 59
- Fluorine, 173
- and oxygen, causes of analogy between, 49
- density, 202
- Flury, F., and A. Gutbier, compounds of sulphur and tellurium, 131
- Fontana, A., and F. M. Perkin, electrolytic oxidation of anthracene, 246
- Fonze-Diacon, and Carquet, M.M., toxicity of nitroprussiate of soda, 226
- volumetric estimation of the alkaline nitroprussiates, and of soluble salts of cadmium, 114
- Ford, J. S., hydrolysis of starch by diastase, 247
- "Fort, Diamond, and Gold Industries of British Guiana, General Information with regard to the" (review), 130
- Formaldehyde and α -tetrahydro- β -naphthylamine, reaction between, 247
- atmospheric, estimation, 311
- polymers of, 298
- solution, action of hydrogen sulphide on, 260
- Forster, M. O., isonitrosocamphor, 295
- and H. M. Attwell, borny-carbamide, 235
- and Frances Mary Gore Mickle, action of nitrogen peroxide on α -nitrocamphene, 92
- Fosse, R., new dinaphthopyranic phenols, 119
- researches on the dinaphthopyranic series, 262
- union of dinaphthopyrrol salts with dialcoholic aromatic amines, 168
- Fournelle, E., certain amino-ethers, 203
- of tertiary alcoholic function, 203
- Fox, J. J., and J. T. Hewitt, studies in the acridine series, 70
- Francis, F. E., and O. C. M. Davis, action of nitrogen sulphide on organic substances, 93
- and Miss Millicent Taylor, additive products of benzylidene aniline with ethylacetacetate and ethyl methylacetacetate, 259
- Francis, M., iodides of mercurammonium of primary and tertiary amines, 34
- Fraps, G. S., report on ash, 41, 54
- Freezing-point curves of dynamic isomerides, 141
- French, W., and L. E. Boardman, "Practical Chemistry" (review), 214
- Freundler, F., reduction of nitrobenzoic acid and acids, 119
- researches on azoic compounds, 22
- transformation of azoic compounds with ortho-substituted alcohols, function into indazolic derivatives, 311
- Friend, J. A. N., estimation of hydrogen peroxide in presence of potassium persulphate by means of potassium permanganate, 177
- Friswell, R. J., intramolecular and originally reversible changes extending over prolonged periods of time, 115, 196, 27
- Furfuraldehyde, condensation with sodium succinate, 83
- Furnace, electric, 307
- Furnaces, muffle and melting, 25
- Fusion with sodium hydroxide, 56
- GADD, H. W.**, "Drugs—their Production, Preparation, and Properties" (review), 142
- Gadolium oxide, preparation of, 238
- Galactose, mutarotation, 246
- Galena, attack of, 56
- Garrett, C. A. B., and P. E. Shaw, coherence and recombination, 285
- Gas, acetylene, application to heating of germination stoves, 215
- coal, part played by benzene in poisoning by, 74
- combustible, given off in the Caspian Sea, analysis, 78
- illumination, determination of benzene in, 14, 29
- occluded in radium bromide, examination, 75
- Gases, action on barium-ammonium, 13
- ammonia, estimation of unburnt products in, 14
- not dissociated by moderate heat, determining percentage of ozone in, 201
- permanent, determination of molecular weight of, 237
- Gautier, D., compounds of saccharose with certain metallic salts, 59, 179
- Gautier, A., degree of accuracy attained in detection of traces of arsenic in organic matters, 226
- norma existence of arsenic in all the organs of the animal economy, 298
- Gayac, oxidation by laccase, 59
- Genessee, P., action of paraformaldehyde on the sesquiterpenes, 2, 8
- Gerard, J., "The Old Riddle and the New Answer" (review), 225
- Getman, F. H., and H. C. Jones, existence of hydrates in concentrated aqueous solutions of α -acetylal, 157
- Gibello, M., and A. Seyewetz, new polymers of formaldehyde, 298
- synthesis of sugars from trioxymethylene and sodium sulphite, 86
- Giesel, F., emanation substance, 267
- Giraud, M., behaviour of phenolphthalein in presence of bicarbonates and alkaline carbonates, 27
- Glass silvering, influence of copper on, 23
- Glabro, R. T., Address to Physical Society, 93
- diffraction theory of the microscope, 213
- Glucuronic chloride, heat of formation, 17
- Glucose, estimation by Fehling solution, sodium monosulphide as an indicator in, 71
- mutarotation, 246, 157
- Glycerides, higher, 175
- Glycerin, phosphoric esters of, 130
- Glycol, phosphoric esters of, 130
- Glycols, primary α -, transformation into corresponding aldehydes, 59
- Godefroy, L., and E. Varenne, ethyl alcohol hydrates, 22
- hydrates of methylic alcohol and acetone, 244
- "Gold and Silver Ores, Cyaniding" (review), 249
- "Gold, Diamond, and Forest Industries of British Guiana, General Information with regard to the" (review), 130
- "Gold Extraction, Cyanide Processes" (review), 142
- Gold analysis, electrolytic, 165
- colloidal, 262
- aqueous solution of, 143
- Goodrich, W. F., "Refuse Disposal and Sewer Production" (review), 285
- Goodson, Ethel Elizabeth, and H. M. Dawson, formation of periodides in nitrobenzene solution, 273
- Goodwin, W., and L. Maquenne phenylurethanes of sugar, 179
- Gordon, J. W., high-power microscopy, 245
- Gorgues, A., baumannites from Sweden, 111
- Gornall, F. H., and F. B. Power, constituents of chaulmoogra seeds, 294
- constitution of chaulmoogric acid, 295
- gynocardin, 295
- Goslings, N., and A. Werner, carbonatopentamine cobaltic salts, 275
- Granger, A., cadmium arsenide, 167
- Green, A. B., radio-activity of bacteria, 215
- A. J., and A. G. Perkins, construction of phenolphthalein, 141
- Grignard, V., action of magnesium and organo-magnesium compounds on bromophenol, 141
- preparation of diethylacetate of methyl, 298
- primary phenylethyl alcohol, 298
- synthesis of tertiary alcohols by means of organo-magnesium compounds, 95
- Grignard's reaction, application to halogen ethers of tertiary alcohols, 275
- Grossmann, H., salts of cadmium, 71
- Guillet, L., constitution and properties of silicon steels, 34
- of vanadium steels, 130
- Guinchant and Christen, M.M., cryoscopic examination of solutions in antimony sulphide, 311
- Guntz, A., La Caze Prize, 58
- and M. Meunier, action of gases on barium-ammonium, 13
- amide and nitride of barium, 34
- Gutbier, A., action of phenylhydrazine on oxidised compounds of selenium and tellurium, 131
- aqueous solution of colloidal gold, 143
- of colloidal selenium, 143
- examination of colloidal sulphides, 59
- gravimetric estimation of tellurium by means of hypophosphorous acid, 143
- quantitative separation of tellurium and antimony, 168
- and E. Flury, compounds of sulphur and tellurium, 131
- and E. Rohu, estimation of selenium, 311
- Guye, P. A., determination of molecular weight of permanent gases, 277
- and E. Mallet, atomic weights of oxygen and hydrogen, 261
- Guyot, A., and A. Haller, action of phenol on potassium bromide on anthraquinone, 130

- Guyot, A., and A. Haller, diphenyl-anthracene and symmetric di-phenyl anthracene dihydride, 310
and Stoebling, M.M., derivatives of tetramethylammoniumphenyl-xanthranol, 107
Gyocardin, 295
- HABER**, F., and M. Stocker, "Praktische Übungen zur Einführung in Die Chemie" (review), 154
Haberg, E., electrolytic estimation of thallium, 311
Hackford, J. E., and H. J. S. Sand, electrolytic estimation of minute quantities of arsenic, 272
Hæmatin, separation of the principles decomposing peroxide of hydrogen contained in the, 6
Haga, T., peroxyaminesulphonates and hydroxylaminetri-sulphonates, 17
Halides of alkali metals, action of cathium rays on, 246
Haller, A., preparation of alcohyl and alcolydic derivatives of cyclic ketones, 286
and G. Blanc, syntheses effected by means of molecules containing the methylene group associated with negative radicals, 59
and A. Guyot, action of phenyl-magnesium bromide on anthraquinone, 130
diphenylanthracene and symmetric diphenylanthracene dihydride, 310
Halogens, action on ethylsodiocarbonylglyutarate, 259
Hamonet, J., halogen ether oxides, 251
preparation of ether oxides by means of magnesium compounds and halogen methyl ethers, 215
Hamy, M., spectrum of zinc, 251
Hann, A. C. O., and A. Lapworth, additive compounds of unsaturated cyclic ketones with hydrogen cyanide, 152
optically active esters of β -ketonic and β -aldehydic acids, 21
Hannay, J. B., higher glycerides, 175
Hanriot, M., colloidal gold, 262
Hanson, E. K., and R. S. Morrell, resolution of α -hydroxybutyric acid into its optically active constituents, 93
Hartley, P., and J. B. Cohen, nitration products of isomeric chlorobenzenes, 297
Hartwell, B. L., behaviour of cerium, lanthanum, neodymium, praseodymium, thorium, and zirconium toward organic bases, 15, 27
Harvey, A. W., phenyldimethylallylammmonium compounds, 177
Hausmannites from Sweden, 211
Hent, action on hydroxycarboxylic acids, 81, 294
on mixtures of phosphorus sesquisulphide and sulphur in carbon disulphide solution, 130
Hebert, A., and E. Charabot, influence of its surroundings on vegetable acidity, 227
and G. Truffaut, chemical study of culture of chrysanthemum, 60
Helbronner, A., derivatives and products of condensation of β -oxy-naphthol aldehyde, 287
Helium, production from radium, 255, 266
Henri, V., and A. Mayer, colloidal solutions, 202
Henriet, H., estimation of atmospheric formaldehyde, 311
formic aldehyde in atmospheric air, 120
Henry, L., methylic ether of acetal, 251
trichloroisopropyl alcohol, 106
T. A., "Aids to Chemistry" (review), 201
Herr, W., simultaneous volumetric estimation of boric acid and strong acids, 60
Hewitt, J. T., and J. J. Fox, studies in the acridine series, 70
J. Kenner, and H. Silk, bromination of phenolic compounds, 272
"Heumann's, Karl, Directions for Lecture Experiments in Inorganic Chemistry" (review), 166
Hibbert, H., and J. J. Sudborough, estimation of hydroxyl radicals, 19
W., magnetic balance, 308
Hiorns, A. J., alloys of copper and arsenic, 200
Holland, H., and C. Baskerville, contributions to the chemistry of the rare earths, 184
Hollard, A., analysis of commercial nickel, 45
applications of the theory of electrostatic separation of metals from one another, 110, 118, 125
influence of physical nature of anode on constitution of electrolytic peroxide of lead, 298
Holmes, J., and T. E. Thorpe, estimation of methyl alcohol in presence of ethyl alcohol, 18
Holroyd, G. W. F., magnesium oxybromide, 115
Homfray, D., and C. T. Kingzett, "Dictionary of Hygiene" (review), 22
Hose of Commons, ventilation, 10
Howard, D., address to the Institute of Chemistry, 128
Howgrave-Graham, R. F., "X-rays Simply Explained" (review), 190
"Human Body, Experiments on the Metabolism of Matter and Energy in" (review), 261
Hydrates in concentrated aqueous solutions of electrolytes, 157
of methylic alcohol and acetone, 244
Hydrazine, use in qualitative analysis, 203
hydrate, vapour density of, 223
Hydrides, halogen, and organic compounds, additive compounds of, 205
ionisation and chemical combination in the liquefied, 294
Hydrindamines, d- and l-, cis-camphanates of, 19
Hydroaromatic series, aromatic compounds obtained from, 93
Hydrocarides, aromatic, action of sulphur and selenium on organo-magnesium compounds of mono- and di-halogen, 251
Hydrocellulose, 17, 235
Hydrogen and chlorine, union, 152, 296
and nickel, finely-divided, direct reduction of aromatic halogen derivatives of, 119
atomic weight, 261, 297
compressibility between one atmosphere and half an atmosphere of pressure, 86
reduction of silicon by, 274
solid, densities of, 205, 217
formation at low temperature, 145
volatilisation of silicon in, 286
cyanide, additive compounds of unsaturated cyclic ketones with, 152
peroxide, estimation in presence of potassium persulphate, 177
separation of the principles composing, contained in the hæmatin, 298
silicide, formation, 261, 286
Hydrogen sulphide, action on formaldehyde and acetaldehyde solutions, 260
ionisation and chemical combination in the liquefied, 294
Hydroxylamine, action of, 23
use in qualitative analysis, 203
Hydroxylaminetri-sulphonates, 17
"Hygiene, Dictionary of" (review), 22
"Hypochlorites and Electrical Bleaching" (review), 46
Hyposulphite, sodic, and iodine, preparation of titrated solutions of, 311
- IGNITION** of material with calcium acetate, 55
with sodium carbonate, 56
Ikeda, K., and J. Sakurai, international atomic weights, 305
"Immune Sera" (review), 310
Imino-ethers and allied compounds corresponding with the substituted oxamic esters, 293
Ince, J., "Latin Grammar of Pharmacy" (review), 46
Inchley, O., and W. E. Dixon, cinnosine, 308
Indaziric derivatives, formation, 22
Indicator, new, 262
Indigo, colouring-matter of, 238
plant fermentation, 296
Inducance, small, standard of, 177
Inductances and capacities, measurement of small, 177
Induction, action of temperature on period of, 152
Insects, living, colour photographs of, 309
Institute of Chemistry, 47, 78, 83, 128, 192, 239
Interference and diffraction, 57
Intramolecular changes, continuous, extending over prolonged periods, 115, 196, 207
"Inventions, Grant and Validity of British Patents for" (review), 142
Iodates, estimation, 95
Iodides of mercur-ammonium of primary and tertiary amines, 34
Iodine and sodic hypsulphite, preparation of titrated solutions of, 311
pure, production, 31
separation from alkaline halogen salts of iodine, chlorine, and bromine, 12
solution in aqueous potassium iodide, 176
Iodine, chemical combination, 294
Ions, complex, influence in electrolysis by alternating currents, 143
Iridium sesquieselenide, preparation, 34
Iron, 173
and alumina, separation, 63
and aluminium, separation, 44, 95
and antimony, separation, 63
and chromium, separation, 183
and cobalt, separation, 280
and nickel, separation, 280
and titanium, separation, 63
and zirconium, separation, 63
estimation in presence of zirconium, 311
formation of peroxides in the case of, 203
meteoric, 34
organisms in Lancashire waters, 8
Irons, determining critical points of, 34
Isomerides, dynamic, freezing-point curves of, 141
Isopropicarlum, fusion with caustic potash, 81
- JACKSON**, H., phosphorescent materials, 245
Jackson, H. A., thermo-chemistry of electrolytic dissociation, 202
W., "Text-book of Ceramic Calculations" (review), 274
Janin, camphor monophenyl, 258
Joffrin, H., application of acetylene gas to heating of germination stoves, 215
John J. Griffin and Sons, Ltd., accurate volumetric apparatus, 240
Jones, C., detection of chlorides in presence of bromides, 229
H. C., "Elements of Inorganic Chemistry" (review), 166
what physical chemistry has done for chemistry, 90, 105
and F. H. Getman, existence of hydrates in concentrated aqueous solutions of electrolytes, 157
H. O., optically active asymmetric nitrogen compounds, 69
and J. Dewar, chemical reactions of nickel carbonyl, 68
Jordis, E., and E. H. Kanter, silicic acid, 251, 263
Joseph, A. F., and J. E. MacKenzie, action of sodium chemistry, 294, and homologues on benzophenone chloride and benzylidene chloride, 72
Jowett, H. A. D., constitution of acetic acid, 92
fusion of isopropylcarpine with caustic potash, 81
Just, A., complex double salt of manganous and tungstic acids, 28
Julau, H. F., and E. Smart, "Cyaniding Gold and Silver Ores" (review), 249
- KANTER**, E. H., silicic acid and the alkaline and alkaline-earthly silicates, 23
and E. Jordis, silicic acid, 251, 263
Kelvin Lord, "Baltimore Lectures" (review), 213
Kenner, J., J. T. Hewitt, and H. Silk, bromination of phenolic compounds, 272
Kerr, R., and A. Smith, microphotography, 245
Ketones, alcolyl-allyl-, 119
allyl- and propenyl-allyl-, 179, 275
boiling-points, 265
cyclic, additive compounds of unsaturated with hydrogen cyanide, 152
preparation of alcolyl and alcolydic derivatives of, 286
Kingdon, J. C., why are some elements so much more abundant than others? 58
Kingzett, C. T., and D. Homfray, "Dictionary of Hygiene" (review), 22
Kipping, F. S., cis-camphanates of d- and l-hydrindamines, 19
organic derivatives of silicon, 81
and A. H. Salway, arrangement in space of groups combined with trivalent nitrogen atom, 116
and F. Tutin, four optically isomeric l-methylamines and their salts, 20
Kirovenagel, E., and E. Ebler, use of hydroxylamine and hydrazine in qualitative analysis, 203
Kling, A., methyl acetate, 251
and M. Viard, differentiation of primary, secondary, and tertiary alcohols of fatty series, 287
Knight, N., precipitation of magnesium oxalate with calcium carbonate, 146
Koppel, J., conditions of formation and solubility of cuprosodic sulphate, 224

- Kouriloff, V., compounds of nitrate of silver with ammonia, 275
- Krauss, L., and E. Rupp, iodometric estimation of copper by means of potassium of potassium, 283
- Krypton, 174
- Kunling, O., "Carl Heumann's Anleitung zum Experimentieren bei Vorlesungen über Anorganische Chemie" (review), 166
- Kunz, G. F., and C. Baskerville, action of radium rays and ultra-violet light on minerals, 1
- Kuster, F. W., and G. Dahmer, precipitation of colloidal solutions of sulphide of arsenic, 215
- L**ABY, T. H., separation of iron from nickel and cobalt by lead oxide, 280
- Lacombe, H., fractionation of the ceric earths, 277
- and U. Urban, europium, 179
- preparation of samaria and atomic weight of samarium, 277
- use of bismuth as a means of separation in rare earth series, 52
- Lactone, oxycrotonic, 262
- Lake, H. B., what may result from the study of radium, 47
- Lamp, mercury-vapour, Bastian, 156
- Landolt, G. D., imino-ethers and allied compounds corresponding with substituted oxamic esters, 293
- Landolt, H., and J. H. Long, "Optical Rotating Power of Organic Substances" (review), 129
- Lanthanates, 173
- Lanthanum, 173
- behaviour towards organic bases, 15, 47
- Lanthanum-alumina, 172
- Lapworth, A., and A. C. O. Haan, additive compounds of unsaturated cyclic ketones with hydrogen cyanide, 152
- optically active esters of β -ketonic and β -aldehydic acids, 21
- Larmor, J., abatement of effects of motion through the ether in relation to constitution of matter, 284
- "Latin Grammar of Pharmacy" (review), 46
- Laurer, A., J. J. Dobbie, and C. R. Finkler, relative strengths of alkaline hydroxides and of ammonia, 17
- Laurel, Californian, essential oil of, constituents, 242
- Laub, C., triphenylmethane colouring matters, 297
- Le Sueur, H. K., action of heat on hydroxycarboxylic acids, 81, 29
- Lead-aluminium alloys, 261
- Lead binoxide, use in analysis, 26
- peroxide, electrolytic, influence of physical nature of anode on constitution of, 278
- salts of monoalkylphosphoric acids, 203
- "Leather Manufacture, Principles of" (review), 166
- Lebeau, F., dissociation of alkaline carbonates, 59
- Leberle, H., and K. Danil, estimation of iron in presence of zirconium, 21
- Leclercq, A., method of separation of aluminium and iron by use of formic acid, 95
- Lees, F. H., derivatives of umbellulone, 224
- and K. B. Fowler, constituents of essential oil of Californian laurel, 224
- Leibmann, A., vacuum drying machinery, 312
- Lemoult, P., action of Cl_2 on cyclic primary amines at boiling-point, 293
- calculating heats of combustion, 12
- calculation of heat of combustion of nitrated organic compounds, 237
- experiments, researches relative to certain cyclic amines, 261
- phospho-nitrated bases, 215
- Leuermann, C., estimation of organic matter in water, 219, 221
- Lespiau, M., chloroacetylacetic ether, 143
- oxycrotonic lactone and γ -substituted crotonic acids, 262
- Lewis, W. H., and P. D. Chattaway, isomeric change of diacylanilides into acylamino-ketones, 176
- Light, action on chlorine, 152
- on mixture of phosphorus sesquiphosphide and sulphur in carbon disulphide solution, 130
- ultra-violet, action on minerals, 1
- Lime, ratio between solubility of and caustification of alkaline carbonates, 298
- sulphate, hydrate 1, solubility in solutions of sea salt, 2
- Limes, oil of, composition of a distilled, 176
- Lindet, L., examination of ancient samples of bread, 199
- inversion of sugar, 156
- Liquid state, 169, 181
- Locke, M., systematic classification of inorganic compounds, 120
- Loccon, R., method of identifying the fatty acids, 311
- London, King's College, 12
- University, position of chemistry in medical curriculum of, 55
- water supply, 52, 84, 146, 211, 242, 314
- Long, J. H., and H. Landolt, "Optical Rotating Power of Organic Substances" (review), 129
- Low, W. H., estimation of adulterant in citroella oil, 12
- Lowe, F. H., and J. C. Crocker, picryl derivatives of urethane and thiourethane, 235
- Lowry, T. M., mutarotation of glucose and of galactose, 246
- Lumière, A. L., and F. Perrin, action of chloracetamide on some aromatic amines, 298
- Lumsden, J. S., new design for chemical balances, 11
- M**CDOWALL, J., volumetric estimation of cyanogen, 229
- McIntosh, D., and E. H. Archibald, basic properties of oxygen, 205
- and J. W. Walker, ionisation and chemical combination in liquefied halogen hydrides and hydrogen sulphide, 294
- J. G., preparing Venetian red, 129
- McKenna, C. F., testing wood treated to resist fire, 32, 40
- McKenzie, A., esterification of γ -methylidic acid by menthol and boron, 116
- Mackenzie, J. E., and A. F. Joseph, action of sodium methoxide and its homologues on benzophenone chloride and benzylidene chloride, 272
- Maclean, W. A., and C. Walker, "Metalurgical Analysis and Assaying" (review), 466
- Machinery, vacuum, 293
- Magnesia cupel, 204
- Magnesium, action on bromophenol, 262
- and nickel compounds, 235
- Magnesium oxalate, precipitation with calcium oxalate, 146
- oxymide, 115
- peroxides, 101
- metry of, 96
- "Magnesium &c. Subject-matter in Library of the Patent Office" (review), 310
- Magnetograph, quartz - thread vertical force, 127
- Magnetostatic field, stresses in a, 128
- Magnets, law of action between, 204
- Malilhe, A., and P. Sabatier, action of reduced nickel on halogen derivatives of fatty series in presence of hydrogen, 143
- cyclohexane and its chlorinated derivatives, 298
- direct reduction of aromatic halogen derivatives by finely divided nickel and hydrogen, 19
- Maillard, L., constitution of the colouring-matter of indigo, 238
- Mallet, E., and P. A. Guye, atomic weights of oxygen and hydrogen, 261
- Mancini, M., formation of peroxides in the case of iron, 203
- Manganese, influences accelerating or retarding action of, considered as a metallic ferment, 12
- oxidation by means of, active influence of albumenoid matter on, 83
- titration, 83
- Mangan - manganates, alkaline earth, 155
- Mannamine, 156
- Mannite and paraldehyde, combinations, 238
- Manosse, new base derived from, 156
- "Manuring of Market Garden Crops" (review), 95
- Maquenne, L., formation and saccharification of retrograde amidon, 101
- retrogradation of amidon starch, 59
- A. Ferbach, and J. Wolff, retrogradation and conjugation of amidon, 71
- and W. Goodwin, phenylurethanes of sugar, 179
- Marc, R., and L. Philippe, ricinine, 156
- Marc, R., decomposition of the final fractions of monazite into components, 232
- Marckwald, W., contributions to our knowledge of radium, 97
- Marshall, A., vapour pressures and properties of hypophosphorous acid, 297
- and L. J. Bunel, estimation of persulphates, 113
- and R. Marcus, action of carbon dioxide on solutions of sodium nitrite, 130
- of carbonic acid on solutions of sodium nitrite, 191
- Marquis, R., and C. Marie, action of carbon dioxide on solutions of sodium nitrite, 130
- of carbonic acid on solutions of sodium nitrite, 191
- Marshall, A., vapour pressures of liquid mixtures of restricted mutual solubility, 296
- J., and J. B. Cohen, reduction of 2:6-dinitroresorcinol with sulphur, 177
- Martin, A. J., "Up to Date Tables of Imperial, Metric, Indian, and Colonial Weights and Measures" (review), 155
- G. G. and C. H. and J. G. G., between fluorine and oxygen, 49
- connection between negative electricity and the valence of atoms, 25
- the volatility of compounds and the chemical forces at play within the molecule, 241
- Martin, G., why are some elements so much more abundant than others? 47, 118
- Martindale, W. H., and W. W. Westcott, "Extra Pharmacopoeia" (review), 309
- Mass action, lecture experiments for demonstration of, 231
- Matignon, C., action of a mixture of oxygen and hydrochloric acid on certain metals, 33
- colour reactions of vanadic acid and ethanol, 52
- and F. Bourion, preparation of anhydrous chlorine, 179
- transformation of oxides and oxygen salts into chlorides, 203
- "Matter and Energy in the Human Body, Experiments on the Metabolism of" (review), 261
- "Matter, Researches on a New Property of" (review), 155
- Matter and radio-activity, 486
- Matthey, E., constant-standard silver trial plates, 124
- Mayer, A., and V. Henri, colloidal solutions, 202
- "Medical and Toxicology, Aids to Forensic" (review), 129
- Melior, J. W., union of hydrogen and chlorine, 152, 296
- Menthyl acetate, condensation with, 21
- Menthylamines, four optically isomeric, 20
- Mentrel and Gunz, M., action of some gases on barium amide, 13
- amide and nitride of barium, 34
- Mercury lamp, estimation, 303
- vapour lamp, Bastian, 156
- Mesoxamide, oxime of, 235
- "Metabolism of Matter and Energy in the Human Body, Experiments on" (review), 261
- "Metalloids" (review), 155
- "Metallurgical Analysis and Assaying" (review), 166
- "Metallurgy, Elementary Text-book" (review), 95
- "Metals, Microscopic Analysis of" (review), 155
- Metals action of a mixture of oxygen and hydrochloric acid on, 35
- alkaline, flame spectra of, 130
- applications of theory of electrolysis to separation of from one another, 110, 118, 125
- hard and soft states in, 307
- specific heat of, 165
- Methyl acetate, saponification, 83, 103
- acetolate, 251
- alcohol, estimation in presence of ethyl alcohol, 235
- diethylacetate, preparation, 298
- tartrate, rotation value at different temperatures, 259
- Methylhydrazine, d., resolution of, 19
- Methylhydrazines, d- and l-, with d-chloroacetylphosphonic acid, isomeric salts of, 151
- Meunier, J., apparatus for regulating the action of vacuum pumps, 191
- history of acetals of polyatomic alcohols of sugar series, 235
- L., action of carbon dioxide on aqueous solutions of aniline in presence of nitrates, 59
- on solutions of sodium nitrite, 151
- Michaëlis, A., and K. von Arend, sub-oxide of phosphorus, and solubility of red phosphorus in alcoholic aqueous pyrosulphic acid, 263
- Mickelthwait, Francis, Henry Gore, and M. O. Forster, action of nitrogen peroxide on i-nitrocamphene, 92

- Mickelthwait, Frances Mary Gore, 31
 T. Morgan, and H. B. Winfield, study of the substitution products of α -tetrahydro- α -naphthylamine, 247
 Micro-manometer, 245
 Microphotography, 245
 Microscope, diffraction theory of, 213
 Microscopes, 94
 Microscopy, high power, 245
 Milk of buffalo cow, sugar in, 262
 Miller, J., and J. B. Cohen, influence of substitution in the nucleus on rate of oxidation of the side-chain, 80
 "Mineral Substances, Treatise on the Analysis of" (review), 155
 "Mineral Tables for the Determination of Minerals by their Physical Properties" (review), 190
 Minerals, action of radium rays and ultra-violet light on, 1 and substances, radio-active, 270
 radio-activity of, 133
 rare, from the Caucasus, chemical analysis of, 123
 Minet, A., electric furnace, 307
 Minguin, J., ethyldene camphor, 168
 Mixtures, liquid, of restricted mutual solubility, vapour pressures of, 296
 viscosity of, 260
 Moissan, H., action of carbon on quicklime at temperature of fusing platinum, 119
 certain physical constants of phosphorus fluorides, 215
 "Classification des Corps Simples" (review), 225
 density of fluorine, 212
 electrolysis of calcium chloride, 297
 preparation of calcium carbide, 126
 presence of argon in the gases of the hot springs of Guadeloupe, 250
 and B. du Jassoneix, density of chlorine, 58
 and F. Siemens, action of silicon on water at a temperature of 100°, 250
 solubility of silicon in zinc and lead, 191
 Moitessier, J., and J. Ville, separation of the principles decomposing peroxide of hydrogen contained in haematite, 298
 Molecular weights, determining, 69
 Molecules containing the methylene group associated with negative radicals, syntheses effected by, 59
 Molybdates and chromates, ammoniacal double, 235
 Monazite, decomposition of final fractions of into components, 122
 Monette, artificial production, 203
 Mono-lithium poly-metha-lanthanate, hydrated, 198
 Mono-sodium poly-metha-lanthanate, hydrated, 198
 Moreau, G., thermic ionisation of saline vapours, 310
 Morgan, G. T., Frances Mary G., Mickelthwait, and H. B. Winfield, study of the substitution products of α -tetrahydro- α -naphthylamine, 247
 Morphine, reaction, 26
 Morrell, R. S., and A. E. Bellars, separation of β -crotonic acid from α -crotonic acid, 140
 and K. H. Hanson, resolution of α - β -dihydroxybutyric acid into its optically active constituents, 93
 Morse, F. W., report on the determination of nitrogen, 232, 241
 Moss, E. G., and C. Baskerville, contributions to the chemistry of the rare earths, 172
 Motor, petrol, projection of the indicator diagrams of, 308
 Moulin, A., colorimetric estimation of chromium, 268
 Mouneyrat, A., elimination and distribution in the organism of medicinal arsenic in form of methylarsenate of soda, 23
 influence of the chemical form under which an element is presented to the organism on the rapidity of its passage into the blood, 24
 Moureu, C., condensation of acetylenic ethers with alcohols, 107
 oxalocetyl-ethylenic carbides and acids, 112
 and R. Delange, amylochloracrylic ethers, 226
 decomposition of acetylenic acids by the alkalis, 226
 general observations on the acetylenic acids, 226
 hydration of the acetylenic acids, 226
 new acetylenic acids, γ , γ' , γ'' -tri-methylbutyric acid, 245
 Mukerjee, B. M., new forms of pipettes, 161
 Murrell, W., "Aids to Forensic Medicine and Toxicology" (review), 129
 Muter, J., "Short Manual of Analytical Chemistry" (review), 47
 NAPHTHALENE, tetrahydro-, series, 247
 Naphthylamine, α -tetrahydro- α , substitution products of, 247
 α -tetrahydro- β - α and formaldehyde, reaction between, 247
 halogen derivatives of, 247
 α -Naphthylmagnesium bromide, action of sulphur and selenium on, 247
 Needham, E. R., and W. H. Perkin, jun., α -nitrobenzoyl-lactic acid, 70
 Neodymium, 158
 behaviour towards organic bases, 157
 alum, attempt to prepare, 185
 chloride solution, saturation with hydrochloric acid, 158
 Neville, A., and R. H. Pickard, reactions on optically active carbimides, 259
 Newell, L. C., "Descriptive Chemistry" (review), 237
 Nickel, and hydrogen, finely divided, direct reduction of aromatic halogen derivatives of, 119
 and iron, separation, 260
 and iron compounds, 235
 commercial, analysis of, 45
 reduced, action on halogen derivatives of fatty series in presence of hydrogen, 143
 carbonyl, chemical reactions of, 68
 Nicotardot, P., separation of chromium and vanadium, 182
 Nitrite, mercuric, and its decomposition by heat, 175
 Nitrocamphene, 1, action of nitrogen peroxide on, 92
 Nitrogen atom, valent, arrangement in space of the groups combined with, 116
 atomic weight, 297
 compounds, optically active asymmetric, 69
 compressibility between one atmosphere and half an atmosphere of pressure, 86
 determination, 282, 291
 estimation, 233
 solid, densities of, 205, 217
 binoxide, action on barium-ammonium, 14
 Nitrogen peroxide, action on iso-nitro-maleic ethers, 311
 on α -nitrocamphene, 92
 sulphide, action on organic substances, 93
 Nitro-isobutylene, 23
 Nitrosocamphor, 180, 295
 Nitrostyrolene, α , reduction of, 23
 Nitrosyl chloride, action on pinene, 271
 Norton, C. L., protection of steel from corrosion, 215
 OBITUARY, Thomas Bayley, 310
 A. W. Williamson, 237
 "Oil Fields of Russia and the Russian Petroleum Industry" (review), 120
 Oil, citronella, estimation of the adulterant in, 21, 82
 essential, of Californian laurel, constituents of, 224
 of lime, distilled, composition, 120
 Oils, thermostat for use in connection with the refractometric examination of, 80
 "Old Kiddle and the Newest Answer" (review), 225
 Olein and ethers, biochemical synthesis, 130
 O'Neill, J. G., and L. M. Dennis, determination of benzene in illuminating gas, 14, 29
 "Ores, Gold and Silver, Cyaniding" (review), 249
 "Organic Substances, Optical Rotating Power of" (review), 129
 Organic bases, weak, precipitation and separation by, 43, 63, 76, 83, 103
 bodies, estimation of halogen atoms in, 82
 compounds, nitrated, heat of combustion, 237
 substances, relation between the chemical composition and the density of their solutions, 117
 Organo-magnesium compounds, action on bromophenol, 262
 on phthalimide and phenylphthalimide, 244
 use in analytical operations, 139
 Osmond, F., and G. Cartaud, meteoric iron, 34
 and J. E. Stead, "Microscopic Analysis of Metals" (review), 154
 Osmosis, electric, in liquid ammonia, 59
 in methyl alcohol, 237, 286
 Ostwald, Wilhelm" (review), 261
 Ostwald, W., elements and compounds, 220
 "Grundriss der Anorganischen Chemie" (review), 261
 and J. H. van't Hoff, "Zeitschrift für Physikalische Chemie" (review), 167
 O'Sullivan, J., comparison of the products of the hydrolysis of potato starch with those obtained from cereal starches, 177
 Oxides, manganese salts as in presence of a colloid, 119
 Oxidation by means of manganese, active influence of albumenoid matter on, 83
 of the side chain, influence of substitution in the nucleus on the rate of, 80
 Oxide, bichloromethyl, symmetric, 275
 canalic, action on barium-ammonium, 14
 compressibility between one atmosphere and half an atmosphere of pressure, 86
 decomposition in blast-furnace, 180
 Oxides, transformation into chlorides, 203
 Oxygen, action on barium-ammonium, 14
 and carbon monoxide, combining volumes of, 223
 atomic weight, 161
 basic properties, 295
 compressibility between one atmosphere and half an atmosphere of pressure, 86
 atomic weight of, 295
 salts, transformation into chlorides, 203
 solid, densities of, 205, 217
 Ozone, action on ethane, 273
 determining percentage in gases not dissociated by moderate heat, 201
 estimation, 243
 PCl₅, action on cyclic primary amines at boiling-point, 298
 Page, T. H., and H. E. Burgess, composition of distilled oil of limes, and a new sesquiterpene, 178
 "Palmer's Workers of the United Kingdom, Directory of" (review), 193
 "Paper Trade Directory" (review), 168
 Paraffin, boiling-points, 265
 Paraformaldehyde, action on sesquiterpenes, 298
 Paraldehyde and mannite, combinations, 238
 Parry, J., "Cyanide Process of Gold Extraction" (review), 142
 Parsons, C. A., demonstration of the autophones, 245
 Patents in Australia, 167
 "Patent Office Library, Subject-list of Works on Electricity, Magnetism, and Electro-technics in" (review), 310
 "Patents for Inventions, British, Grant and Validity of" (review), 142
 Paterson, J. W., relative effects of superphosphates and basic slag upon the feeding quality of swedes, 131
 Patterson, T. S., comparison of the rotation values of methyl-, ethyl-, and α -propyl-tartrates at different temperatures, 259
 influence of solvents on rotation of optically active compounds, 297
 Peachey, S. J., and W. J. Pope, preparation of tetra-alkyl derivatives of stannimethane, 20
 Pecqueur, H., lead-aluminium alloys, 261
 "Properties of tin-aluminium alloys," 286
 zinc-aluminium alloys, 247
 Peabon, H., fusibility of mixtures of bismuth protosulphide and antimony sulphide, bismuth protosulphide and antimony sulphide, 12
 mixtures of antimony trisulphide and antimony, 119
 Penic, astigmatism, 27
 Pencils, non-homocentric, and shadows produced by them, 57, 153
 Periodides, formation in nitrobenzene solution, 273
 in organic solvents, 152
 Perkin, A. G., and A. G. Green, constitution of phenolphthalein, 141
 and F. M. Perkin, electrolytic oxidation of phenols, 92
 and S. Phipps, natural colouring matters, 18
 F. M., and A. Fontana, electrolytic oxidation of anthracene, 236
 Oxides, transformation into chlorides, 203
 Oxygen, action on barium-ammonium, 14
 and carbon monoxide, combining volumes of, 223
 atomic weight, 161
 basic properties, 295
 compressibility between one atmosphere and half an atmosphere of pressure, 86
 atomic weight of, 295
 salts, transformation into chlorides, 203
 solid, densities of, 205, 217
 Ozone, action on ethane, 273
 determining percentage in gases not dissociated by moderate heat, 201
 estimation, 243
 PCl₅, action on cyclic primary amines at boiling-point, 298
 Page, T. H., and H. E. Burgess, composition of distilled oil of limes, and a new sesquiterpene, 178
 "Palmer's Workers of the United Kingdom, Directory of" (review), 193
 "Paper Trade Directory" (review), 168
 Paraffin, boiling-points, 265
 Paraformaldehyde, action on sesquiterpenes, 298
 Paraldehyde and mannite, combinations, 238
 Parry, J., "Cyanide Process of Gold Extraction" (review), 142
 Parsons, C. A., demonstration of the autophones, 245
 Patents in Australia, 167
 "Patent Office Library, Subject-list of Works on Electricity, Magnetism, and Electro-technics in" (review), 310
 "Patents for Inventions, British, Grant and Validity of" (review), 142
 Paterson, J. W., relative effects of superphosphates and basic slag upon the feeding quality of swedes, 131
 Patterson, T. S., comparison of the rotation values of methyl-, ethyl-, and α -propyl-tartrates at different temperatures, 259
 influence of solvents on rotation of optically active compounds, 297
 Peachey, S. J., and W. J. Pope, preparation of tetra-alkyl derivatives of stannimethane, 20
 Pecqueur, H., lead-aluminium alloys, 261
 "Properties of tin-aluminium alloys," 286
 zinc-aluminium alloys, 247
 Peabon, H., fusibility of mixtures of bismuth protosulphide and antimony sulphide, bismuth protosulphide and antimony sulphide, 12
 mixtures of antimony trisulphide and antimony, 119
 Penic, astigmatism, 27
 Pencils, non-homocentric, and shadows produced by them, 57, 153
 Periodides, formation in nitrobenzene solution, 273
 in organic solvents, 152
 Perkin, A. G., and A. G. Green, constitution of phenolphthalein, 141
 and F. M. Perkin, electrolytic oxidation of phenols, 92
 and S. Phipps, natural colouring matters, 18
 F. M., and A. Fontana, electrolytic oxidation of anthracene, 236

- Perkin, F. M., and W. C. Prebble, electrolytic analysis of gold, 165
- W. H., jun., experiments on the synthesis of the terpenes, 223
- Phenylacetylenic acid, 141
- and E. R. Needham, *o*-nitrobenzoylacetic acid, 70
- and Alice Emily Smith, *cis*- and *trans*-modifications of *o*-methylglutaconic acid, 80
- Permanganate, *E*, *r*, *u*, *u*, *u*, 33
- Peroxide, nitric, constitution, 18
- Peroxides, formation in case of iron, 203
- Peroxyammonium sulphates, 17
- Perrin, P., and A. L. Lumière, action of chloracetamide on some aromatic amines, 293
- Persulphates, estimation, 118
- Pesci, L., organo-metallic compounds of benzoic acid, 83
- Petit, J., and A. Brochet, influence of complexions in electrolysis by alternating currents, 143
- use of alternating currents for electrolysis, 130
- Petroleum Aids, 263
- "Pharmacy, Latin Grammar of" (review), 46
- "Pharmacy, Year-book of" (review), 21
- "Phase Rule and its Applications" (review), 201
- Phase rule, application to precipitation of cobalts, 202
- Phenol and disulphides, limit of union, 311
- tri-iodine, 34
- Phenolic compounds, bromination, 272
- Phenolphthalein, behaviour in presence of bicarbonates and of alkaline carbonates, 27
- constitution, 141
- Phenols, calicheptin, 119
- electrolytic reduction, 92
- Phenyl carbamate, chloruration in presence of antimony chloride, 251
- in presence of iodine, 238
- Phenyl dimethyl ammonium compounds, 177
- Phenylhydrazine, action on oxidised compounds of selenium and tellurium, 131
- and cerium, 64
- and ferric salts, 65
- and thorium, 64
- hydrochloride, hydrolysis, 77
- Phenyl migration, 22
- Phenylmagnesium bromide, action on anthraquinone, 130
- of sulphur and selenium on, 239
- Phenylphthalimide, action of organo-magnesium compounds on, 24
- Phillips, L., and L. Maquenne, ricinine, 156
- Phillips, C. E. S., automatic gas pump, 213
- vacuum pump, 308
- Phipps, E., and A. G. Perkin, natural colouring matters, 18
- Photographic transparencies, three-colour, illumination by spectrum colours, 212
- Phosphate, dicalcic, 203
- trimethyl-amino-magnesium, 34
- trimethylamino-magnesium, 34
- Phosphates, amino-magnesium, 34
- Phospho-nitrate bases, 215
- Phosphorescent materials, 245
- Phosphorus and sulphur, 54
- compounds, organic, 116
- red, solubility in alcoholic aqueous potash, 263
- fluorides, physical constants of, 215
- sesquisulphide and sulphate, action of heat and light on mixtures of in carbon disulphide solution, 100
- sub-oxide, 203
- sulphides, formation in the cold, 130
- Phthalimide, action of organo-magnesium compounds on, 244
- Physical Society, 57, 93, 127, 153
- 177, 212, 240, 284, 306
- Address to, 93
- Physiology, 300
- Pickard, R. H., and A. Neville, optically active carbamides, 259
- Piling, normal, as connected with Osborne Reynolds's theory of the universe, 212
- Pineal and pinecone, reactions of, 35
- Pineole, action of nitrosyl chloride on, 271
- Piperidine urethanes, phenolic, 238
- Pipettes, 161
- Planes, P., colorimetric estimation of bismuth, 10
- Plant, indigo, fermentation, 296
- Plants, chlorine in, 35
- Platinum aulides, preparing, 274
- Platinum solution, electrolytic, 274
- Plimmer, R. H. A., separation and estimation of silver cyanide and silver chloride, 19
- Polarisation, cathodic, 239
- Pollard, C. E., colouring varnish, 264
- Pollard, J. H., heat of formation of glucinum chloride, 176
- Pope, W. J., and S. J. Peachey, preparation of tetra-alkyl derivatives of stannimethane, 20
- Forcher, C., sugar in milk of buffalo cow, 203
- and M. Brissac, attempts to make aniline and urea take the form of amino-magnesium phosphate, 35
- some amino-magnesium phosphates, 34
- Potash, alcoholic aqueous, solubility of red phosphorus in, 263
- calcic, fusion of isopropylcarbinol with, 81
- determination, 54
- Potassium ferrocyanide and potassium ferricyanide, chemical equilibrium between in presence of alkalis, 254
- iodide, aqueous, nature of a solution of iodine in, 176
- permanganate and oxalic acid, speed of reaction between, 96
- Potter, H., biochemical synthesis of olein and certain ethers, 130
- Power, F. B., and F. H. Gornall, constituents of chaulmoogric seeds, 244
- constitution of chaulmoogric acid, 295
- gynoacid, 295
- and F. C. Lee, constituents of essential oil of Californian laurel, 224
- and F. Lutin, levorotatory modification of quercitol, 223
- Pozzo, E. T. E., colour reactions of molybdate, 106
- Præodinium, 147
- behaviour toward organic bases, 15, 27
- nitram, attempt to prepare, 184
- citrale, 148
- Prebble, W. C., and F. M. Perkin, electrolytic analysis of gold, 165
- Precipitation and separation by weak organic bases, 43, 63, 76, 88, 103
- Printing, application of thin-film electrolysis to, 105
- Procter, H. K., "Principles of Leather Manufacture" (review), 166
- n*-Propyl, ethyl, and methyl tartrates, rotation values at different temperatures, 459
- Propylisocinchonate carbonate, 143
- Prud'homme, M., chemical equilibrium between ferro- and ferricyanide of potassium in presence of alkalis, 254
- between ferro- and ferric-hydrocyanic acids, 199
- Pump, gas, automatic, 213
- vacuum, automatic, 300
- Pumps, vacuum, apparatus for regulating action of, 191
- Pyridic bases, action of bromosuccinic and dibromosuccinic acid on, 34
- QUERCITOL, levorotatory modification of, 223
- Quicklime, action of carbon on at the temperature of fusing platinum, 119
- Quinolic bases, action of bromosuccinic and dibromosuccinic acid on, 34
- RADIATION, Röntgen, energy of secondary, 172
- Radicles, hydrolytic, estimation, 19
- Radio-active minerals and substances, 270
- "Radio-activity" (review), 309
- Radio-activity and matter, 289
- induced, 289
- of bacteria, 245
- of minerals and mineral waters, 133
- "Radio and All about it" (review), 250
- Radium, 33, 97, 174
- and barium, separation, 97
- emanation, spectrum of, 301
- production of helium from, 255, 269
- rays, action on halides of alkali metals, 246
- on minerals, 1
- photographic action of, 58
- what may result from the study of, 47
- barium chloride, anhydrous, phosphorescence of, 97
- bragade, examination of sample of gas evolved in, 85
- Ramage, H., boiling-points of homologous compounds, 265
- distribution and spectra of metallic vapours in electric arcs, 263
- Ramsey, Sir W., "Introduction to the Study of Physical Chemistry" (review), 154
- and J. N. Collie, spectrum of radium emanation, 301
- and F. Soddy, further experiments on production of helium from radium, 255, 266
- Rape, green, distribution of sulphur in, 55
- Raper, H. S., J. T. Thompson, and J. B. Cohen, action of sodium hypochlorite on aromatic sulphonamides, 153
- Ray, E. C., mercuric nitrate and its decomposition by heat, 175
- Rayleigh, Lord, compressibilities of oxygen, hydrogen, nitrogen, and carbonic oxide between one atmosphere and half an atmosphere of pressure, 86
- Red, Venetian, preparing, 197
- "Refuse disposal and Power Production" (review), 285
- Rengade, A., action of carbonic acid on ammonium metals, 179
- "Report on Agricultural Work in Botanic Gardens and Government Laboratory at British Guiana" (review), 274
- Report of International Committee on atomic weights, 68, 164, 173
- on ash, 4, 54
- on determination of nitrogen, 282, 291
- Reverdin, J., and P. Crepeux, nitration of acetylglucoside, 287
- Reynolds, O., normal piling as connected with theory of the universe of, 212
- Richards, J. W., thermo-chemistry of theory of electrolytic dissociation, 31, 37
- and V. Engelhardt, "Electrolysis of Water" (review), 214
- Ricinine, 156
- Rimini, E., new reaction for aldehydes, 131
- Ringer, W. E., mixed crystals of sulphur and selenium, 131
- Rivoli, marks, origin and growth, 308
- Rivals, P., and H. Baubigny, separation of iodine from alkaline halogen salts of iodine, chlorine, and bromine, 15
- Rivot's method of estimation of iron in presence of zirconium, 311
- Roberts, J., "Grant and Validity of British Patents for Inventions" (review), 142
- W., and J. J. Sudborough, diortho-substituted benzoic acids, 19
- Robinson, L., new indicator, 262
- Roe, S., camphor monopoly in Japan, 250
- Robn, E., and A. Gutbier, estimation of selenium, 311
- Romy, J., and J. A. Voorhies, estimation of formic aldehyde in air, 23
- Röntgen radiation, energy of secondary, 178
- Roscoe, Sir G., address to, 222
- Roscoe, J. K., properties of silver-cadmium series of alloys, 86
- Roux, E., mannamine, 156
- Royal Institution, 24, 58, 71, 95, 130, 131, 145, 179, 192, 209, 220, 229, 254, 276
- Society conversations, 245, 308
- Rubidium, atomic weight, 243
- Kuff, O., and G. Winterfeld, bromides of sulphur, 287
- Rutemann, S., and E. K. Watson, contributions to knowledge of β -diketones, 140
- Rupp, E., iodometric estimation of thallium, 24
- iodometry of the peroxides of calcium, strontium, barium, magnesium, and sodium, 96
- and L. Kraus, iodometric estimation of copper by means of zinc, 263
- and O. Schaumann, iodometric estimation of bismuth in the form of chromate, 143
- "Russia, Oil Fields of, and the Russian Petroleum Industry" (review), 120
- Rutherford, E., "Radio-activity" (review), 309
- SABATIER, P., and A. Mailhe, action of reduced nickel on halogen derivatives of fatty acids, 143
- cyclohexane and its chlorised derivatives, 298
- direct reduction of aromatic halogen derivatives of fully-divided nickel and hydrogen, 143
- and J. B. Senderens, direct hydrogenation of aniline, 155
- of homologues of aniline, 310
- preparation of cyclohexanol and cyclohexanone from phenol, 33
- Saccharine, detection by new reactions, 132
- Saccharose and metallic salts, composition, 59, 179
- Sack, M., formation of alloys of sodium and their importance in phenomena of cathodic polarisation, 239
- St. Bogdan, M., use of bromide of lead in analysis, 26
- Sakurai, J., and K. Ikeda, international atomic weights, 305
- Salt of manganous and tungstic acids, complex double, 288
- Salter, C. I. C., and Dr. von Schwartz, "Fire and Explosion Risks" (review), 286
- Salts, carboxybenzotetramine cobaltic, 272
- disulphide, electrolytic, union with dialcyclic aromatic amines, 168

- Salts.** ferric, and phenylhydrazine, 65
 formation from diortho-substituted benzoic acids and organic bases, 19
 isomeric, of *d*- and *l*-methylhydramidines with *d*-chloro-camphorsulphonic acid, 19
 magnesium, as oxydes in presence of a colloid, 119
 metallic, and saccharose, compounds, 59, 179
 of lower fatty acids, solubility, 19
 oxygen, transformation into chlorides, 203
d- and *l*-phenylbenzylmethyl-ethylammonium, 69
 silver and lead, of monoalcoylphosphoric acids, 203
 Salway, A. H., and F. S. Kipping, arrangement in space of groups combined with ter-valent nitrogen atom, 116
 Samaria, preparation, 277
 Samarium, 234
 atomic weight, 277
 Sand, H. J. S., and J. E. Hackford, electrolytic estimation of minute quantities of arsenic, 272
 Sazercz, R., oxidising bacterium, 287
 Schenk, R., and P. Zimmermann, decomposition of carbonic oxide in blast-furnace, 180
 Scott, A., combining volumes of carbon monoxide and oxygen, 223
 vapour density of hydrazine hydrate, 223
 Sea-salt, solubility of hydrated sulphate of lime in solutions of, 94
 Seeds, chaalmoogra, constituents, 29
 Selenium, action on bromides of phenyl-magnesium and α -naphthylmagnesium, 239
 on organo-magnesium compounds of mono- and di-halogen aromatic hydrocarbides, 251
 and sulphur crystals, mixed, 131
 and tellurium, oxidised compounds of, action of phenylhydrazine on, 131
 colloidal, aqueous solutions of, 143
 estimation, 311
 Senderens, J. B., and P. Sabatier, direct hydrogenation of aniline, 155
 of homologues of aniline, 310
 preparation of cyclohexano and cyclohexanone from phenol, 33
 Sensitometers, colour, calculation of colours for, 212
 Sesquiterpene, composition of a new, 176
 Sesquiterpenes, action of paraformaldehyde on, 293
 Sexton, A. H., "Elementary Text-book of Metallurgy" (review), 95
 Seyewetz, A., and M. Gibello, new polymers of formaldehyde, 298
 synthesis of sugars from trioxymethylene and sodium sulphite, 86
 Shadows produced by axially symmetrical bodies, possessing spherical aberration, 153
 Shafts, whirling and transverse vibrations of, 153
 Shaw, P. E., and C. A. B. Garrett, coherence and recobherence, 285
 Sheridan, F., physiotype, 308
 Sherman, H. C., sulphur and phosphorus, 54
 Shrivell, F. W. E., and B. Dyer, "Manufacturing of Market Garden Crops" (review), 95
 Side-chain, influence of substitution in nucleus on the rate of oxidation of, 80
 Siemens, F., and H. Moissan, action of silicon on water at a temperature of 100° , 250
 solubility of silicon in zinc and lead, 191
 Silberrad, O., action of ethylic β -iodopropionate on ethyl di-sodioethane-tetracarboxylate, 176
 and T. H. Easterfield, ethyl carboxylate, 259, 266
 silica, colorimetric, determination of small quantities, 73, 89, 101
 Silicates, alkaline and alkaline-earthly, and silicic acid, 23
 reduced, 235
 Silicon, action on water at a temperature of 100° , 250
 derivatives, organic, 181
 reduction by hydrogen, 274
 solubility in zinc and lead, 191
 solubilisation in hydrogen, 286
 Silk, H. J., T. Hewitt, and J. Kenner, bromination of phenolic compounds, 272
 "Silver and Gold Ores, Cyanidation" (review), 249
 Silver, colloidal, preparation and properties of pure, 218
 trial-plates, constant standard, 124
 cadmium series of alloys, properties of, 86
 chloride and silver cyanide, separation and estimation, 19
 compounds, 275
 salts of monoalcoylphosphoric acids, 203
 sulphide and bismuth protosulphide, fusibility of mixtures, 275
 Simmonds, C., reduced silicates, 235
 Simon, L. J., diurides, 130
 glycolic urea, 133
 homoalcoholic ether, 130
 new action of hydroxyamine, 22
 and A. Conduche, new reaction of aldehydes, 251
 Simonet, A., combination of hexatomic alcohols with mononitrobenzaldehyde, 23
 and L. Vignon, action of diazobenzene chloride on diphenylamine, 275
 Skinner, S., photographic action of radium rays, 58
 Slag, basic, and superphosphate, relative effects upon the leaching quality of swedes, 131
 Smart, E., and H. F. Julian, "Cyaniding Gold and Silver Ores" (review), 249
 Smith, A., "Laboratory Outline of General Chemistry" (review), 249
 A., and R. Kerr, microphotography, 245
 Alice Emily, and W. H. Perkin, jun., cis- and trans-diolactone acid, 80
 C., tetrahydronaphthalene series, 247
 N., gaseous carbon monosulphide described by Thomsen, 25
 Soda carbonate to precipitate lime and magnesia for chemical purification of water, 254
 nitroprussiate, toxicity of, 226
 Soddy, F., and Sir W. Ramsay, further experiments on production of helium from radium, 255, 266
 Sodeau, W. H., estimation of unburnt products in chimney gases, 61
 Sodium alloys, formation, 239
 acetylacetone, action of epichlorohydrin on, 59
 carbonate, ignition with, 56
 hydroxide, fusion with, 56
 hypochlorite, action on aromatic sulphonamides, 153
 methoxide, action on benzophenone chloride and benzyldichloride, 272
 Sodium monosulphide as an indicator in estimation of glucose by Fehling solution, 71
 nitrate solutions, action of carbon dioxide on, 139, 155
 of carbonic acid on, 191
 percarbonate, 165
 peroxide, iodometry of, 96
 succinate, condensation of furfuraldehyde with, 80
 sulphite and trioxymethylene, synthesis of sugars from, 86
 Soil analysis, rapid, 183
 Soils, scale for chemical valuation, 197
 Solids, formation at low temperatures, 145
 "Solution, Treatise on the Theory of" (review), 191
 Solutions, colloidal, 202
 in antimony sulphide, cryoscopic examination of, 311
 Solvents, influence on rotation of optically active compounds, 297
 Sommelet and Behal, MM., method of synthesis of aldehydes, 83
 Sorel, E., "La Grande Industrie Chimique Minérale" (review), 46
 Southerden, F., conversion of isopropyl alcohol into isopropyl ether by sulphuric acid, 261
 separation of iron and chromium, 183
 Sower, R. J., portable electroscope, 128
 Sparks, electric, distribution and spectra of metallic vapours in, 253
 Specific heat of metals, 165
 relation to atomic weight, 165
 Spectra, absorption, of solutions of salts of didymium containing phosphoric acid, 299
 flame, of the alkaline metals, 130
 of metallic vapours in electric sparks, 253
 Spectrum of the radium emanation, 301
 of zinc, 251
 spark and arc, of zinc, invariability of the wave lengths in, 251
 Spencer, A., and J. W. Walker, compounds of aluminum chloride with organic substances containing oxygen, 29
 J. B., and A. W. Titherley, condensation of furfuraldehyde with sodium succinate, 80
 Spica, M., detection of saccharine by new reactions, 132
 Sprankling, C. H. G., W. A. Bone, and J. J. Sudborough, acid esters of methylsuccinic acid, 177
 Stacheyne, 287
 Staehelin, R., part played by benzene in poisoning by coal-gas, 74
 Stanley, H., solubility of some salts of lower fatty acids, 193
 Stannumethane, preparation of tetra-allyl derivatives of, 20
 Starch, amylon, retrogradation of, 177
 hydrolysis by diastase, 247
 potato, comparison of products of hydrolysis of with those obtained from cereal starches, 177
 composition, 132
 Stead, J. E., and F. Osmond, "Microscopic Analysis of Metals" (review), 154
 Steel, protection from corrosion, 215
 Steels, determining the critical points of, 34
 nickel, allotropic transformations of, 139
 silicon, constitution and properties, 34
 vanadium, constitution and properties, 130
 Stern, A. I., so-called hydrocellulose, 117
 Stevenson, R., and C. Baskerville, contributions to the chemistry of the rare earths, 158
 Stokings, W. E., and W. A. Bone, slow combustion of ethane, 246
 and J. Drugman, action of hydrogen sulphide on formaldehyde and acetaldehyde solutions, 260
 Stoeker, M., and F. Haber, "Praktische Übungen zur Einführung in die Chemie" (review), 154
 Stoecking and Guyot, MM., certain derivatives of tetramethylidiaminophenylloxanthranol, 107
 Stolzenberg system of keeping notes, 269
 Storbeck, O., and G. Bodlander, study of cuprous compounds, 59
 Stoves, germination, application of acetylene gas to heating of, 215
 Stresses in a magnetostatic field, 128
 Strontium peroxides, iodometry of, 269
 Strutt, R. J., radio-activity of minerals and mineral waters, 133
 Sudborough, J. J., and H. Hibbert, estimation of hydroxyl radicals, 19
 and W. Roberts, diortho-substituted benzoic acids, 19
 W. A. Bone, and C. H. G. Sprankling, acid esters of methylsuccinic acid, 177
 Sugar in milk of buffalo cow, 262
 inversion, 156
 phenylurethanes, 179
 Sugars from trioxymethylene and sodium sulphite, synthesis, 86
 Sulphate, cuprosodic formation and solubility, 224
 Sulphates, determination, 54
 double, 172, 174
 Sulphides, colloidal, examination of, 59
 Sulphonamides, aromatic, action of sodium hypochlorite on, 153
 Sulphur, action on bromides of phenylmagnesium and α -naphthylmagnesium, 239
 on organo-magnesium compounds of mono- and di-halogen aromatic hydrocarbides, 251
 and phosphorus, 54
 sesquisulphide, action of heat and light on mixtures of in carbon disulphide solution, 130
 and selenium crystals, mixed, 131
 and tellurium compounds, 131
 determination, 41, 54
 in green rape, distribution, 55
 bromides, 287
 Superphosphate and basic slag, effects upon feeding quality of swedes, 131
 Sutherland, W. G., "Dispensing made Easy" (review), 142
 Sweden, haugmannite, 211
 Swedes, effects of superphosphate and basic slag upon the feeding quality of, 131
 Swinburne, J., "Entropy" (review), 225
 Syntheses by means of molecules containing methylene group associated with negative radicals, 59
 ("TABLES. Calculating" (review), 214
 "Tables of Imperial, Metric, Indian and Colonial Weights and Measures, Up to Date" (review), 155

- Taboury, F., action of sulphur and selenium on bromide of phenylmagnesium and bromide of α -naphthylmagnesium, 238
- on organo-magnesium compounds of mono- and di-halogen aromatic hydrocarbons, 251
- Tanatar, S., percarbonate of sodium, 168
- Tannin and bismuth compounds, 239
- Tanret, C., stachyose, 287
- tar distilleries, accidents in, 35
- Tartrate, crystalline chromous, 207
- Tartrates, optical activity in aqueous solution, 287
- Tattersall, G., isomeric salts of *d*- and *l*-methylhydramines with *d*-chloroamphorsulphonic acid, 19
- resolution of *d*-methylhydramine, 19
- Taylor, Millicent, and P. E. Francis, additive products of benzylidenecyanine with ethyl acetate and ethyl methylacetate, 259
- Tchernik, G. P., chemical analysis of two rare minerals from the Caucasus, 123
- Tchougacff, L. A., use of organo-magnesium compounds in analytical operations, 139
- Technical research and the college system, 230
- "Technics" (review), 240
- Telephone cable, propagation of alternating current along, 306
- Tellurium, 174
- and antimony, separation, 168
- and selenium, oxidised compounds of, action of phenylhydrazine on, 131
- and sulphur compounds, 131
- estimation, 143
- Temperature, action on period of induction, 152
- Terpenes, synthesis of, 223
- Tetrahedral, synthesis of, 223
- Terpinole, inactive, synthesis of, 223
- Tetraphenylmethane series, 247
- of Tetraphenyl- α -naphthylamine, substitution products of, 247
- Tetramethylaminophenylloxan- α -thranol derivatives, 107
- Tetramethylene series, synthesis of, 251
- Thallium estimation, 24, 311
- Thermostat for use in connection with refractometric examination of oils and fats, 80
- Thibault, P., action of hydrated oxide of bismuth on acid isomers of gallic acid, 227
- compounds of bismuth and tannin, 238
- some compounds by means of which the constitution of bromothallic acid may be determined, 23
- Thiel, A., simplification of the method for estimation of zinc in the form of sulphide, 16
- Thienobenzoylacetone, 23
- Thiocarbamide, 141
- Thiouretane, picryl derivatives, 235
- Thompson, A. B., "Oil Fields of Russia and the Russian Petroleum Industry" (review), 120
- Thompson, J. T., H. S. Raper, and J. B. Cohen, action of sodium hypochlorite on the aromatic sulphonic acids, 153
- W. P. and Co., Australian Patent law, 167
- Thomsen, M., gaseous carbon monosulphide described by, 25
- Thorium and beryllium, separation, 77
- and phenylhydrazine, 64
- behaviour toward organic bases, 15, 27
- Thorpe, T. E., interdependence of the physical and chemical criteria in analysis of butter fat, 80
- thermostat for use in connection with refractometric examination of oils and fats, 80
- and J. Holmes, estimation of methyl alcohol in presence of ethyl alcohol, 18
- Threlfall, K., micro-manometer, 239
- Tiffeneau, M., phenylic migration, 22
- transformation of primary α -glycols into the corresponding aldehydes, 51
- two isomeric β -methylcinamic acids, 251
- Tilden, W. A., action of nitrosyl chloride on pinene, 271
- Address to Chemical Society, 190
- specific heats of metals, and relation of specific heat to atomic weight, 165
- "Times Engineering Supplement" (review), 251
- Tin-aluminum alloys, property of, 286
- Tinker, C. K., J. J. Dobbie, and A. C. Smith, estimation of the alkaline strengths of ammonia as measured by their action on cotinine, 17
- Titanium and beryllium, separation, 77
- and iron, separation, 63
- Thierher, A. W., and J. F. Spencer, condensation of furfuraldehyde with sodium succinate, 80
- "Tokyo Imperial University of Calendar" (review), 249
- Toluenes, mono- and dichloro-, oxidation, 85
- Tomkins, D., effect of thermic constants, and heat of formation of compounds of barium, 123
- new electric accumulator, 287
- "Toxicology and Medicine, Aids to Forensic" (review), 129
- Travels, M. W., formation of solids at low temperatures, 145
- Trial-plates, constant-standard silver, 124
- Trilla, L. G., active influence of albumenoid matter on oxidation by means of manganese, 83
- influences accelerating or retarding action of manganese considered as a metallic ferment, 12
- manganous salts as oxydases in presence of a colloid, 119
- Triphenylmethane and sodium sulphite, synthesis of sugars from, 86
- Triphenylmethane colouring matters, 267
- Trilla, L. G., and A. Hébert, chemical study of the culture of chrysanthemums, 60
- Tube, safety, new, 262
- Turpetine essence from Landes, 262
- Turentine, J. W., and C. Baskerville, contributions to chemistry of rare earths, 147
- Tutin, F., and F. B. Power, levorotatory modification of quercitol, 223
- and F. S. Kipping, four optically isomeric *l*-methylamines and their salts, 20
- ULKE, T., and V. Engelhardt, "Die Elektrolytische Raffination des Kupfers" (review), 225
- Umbellulone derivatives, 224
- Universe, theory of, normal piling as connected with, 212
- Uroch, V., constants of sulphide of carbon, 83
- and M. Erdmann, yellow arsenic, 71
- Uranium nitrate, precipitation of, 256
- Urban, G., and H. Lascombe, curium, 179
- preparation of samaria and atomic weight of samarium, 272
- use of bismuth as a means of separation in the rare earth series, 52
- Urea, attempt to make the form of anino-magnesium phosphate, 35
- Urethres, glyoxyl, 143
- Urethane, picryl derivatives, 235
- Urethanes, phenolic, of piperidine, 235
- VACUUM drying machine, 312
- machinery, 258
- Vailant, V., thienbenzoylacetone, 23
- Valente, E., and J. M. Eder, invariability of the wave lengths in spectra and arc spectrum of zinc, 99
- Van't Hoff, J. H., and W. Ostwald, "Zeitschrift für Physikalische Chemie" (review), 167
- Vanadium and chromium, separation, 182
- Vapour pressures of liquid mixtures of restricted mutual solubility, 296
- Vapour, metallic, in electric sparks, distribution and spectra, 253
- saline, thermic ionisation, 310
- Varenne, K., and L. Godefroy, ethyl alcohol hydrates, 22
- hydrates of methyl alcohol and acetone, 244
- Varnish, colouring, 264
- Vegetable acid, influence of its surroundings on, 227
- Vetch, F. P., colorimetric determination of small quantities of phosphoric acid and silica, 73, 89, 101
- Venel and red, preparing, 197
- Ventilator, the House of Commons, 168
- Vezes, M., estimation of essence of turpentine from Landes, 287
- Viard, M., and A. Kling, differentiation of primary, secondary, and tertiary alcohols of fatty series, 287
- Vibograph, 245
- Vignon, L., determination of carbonate of sodium necessary to precipitate lime as a magnesia for the chemical purification of water, 254
- infusible copper on silvering of glass, 23
- limit of the union of diazobenzene and phenyl, 311
- and A. Simonet, action of diazobenzene chloride on diphenylamine, 275
- Vigouroux, E., formation of hydrogen silicide, 286
- Vigreux, H., washer and safety tube, 262
- Ville, J., and J. Moiteissier, separation of principles decomposing peroxide of hydrogen contained in hæmatin, 295
- Viscosity, 256
- of liquid mixtures, 260
- Volatility of compounds and chemical forces at play within the molecule, connection between, 241
- Von Aend, K., and A. Michaelis, solubility of red phosphorus in aqueous aqueous potash, 263
- Von Liester, A., and L. Wolfer, lecture experiments for the demonstration of mass action, 231
- Von Schwartz, Dr., and C. T. C. Sauer, "Fire and Explosion Risks" (review), 286
- Voorhans, J. A., and G. Romijn, estimation of benzoic benzoide in the air, 25
- WADMORE, J. M., and F. D. Chatterjee, derivatives of highly-substituted anilines, 84
- Wagner, A., absorption spectra of solutions of salts of didymium containing phosphoric acid, 249
- Wahl, A., and L. Passmann, action of peroxide of nitrogen on ionospheric anions, 317
- gradual synthesis of the fatty aldehydes, 226
- nitro-isobutylene, 23
- preparation of diketonic ethers, 249
- reduction of α -nitro-styrene, 23
- Wakort, C. D., radio-active minerals and substances, 270
- Walden, P., "Wilhelm Ostwald" (review), 167
- Walker, C., and W. A. Macleod, "Metallurgical Analysis and Assaying" (review), 166
- G. W. stresses in a magnetostat, 259
- J. Introductory to Physical Chemistry" (review), 214
- J. W., ionisation and chemical combination, 294
- and A. Spencer, compounds of aluminum chloride with organic substances containing oxygen, 294
- D. McIntosh, and E. H. Archibald, ionisation and chemical combination in the liquefied halogen hydrides and hydrogen sulphide, 294
- Washer, 262
- Wassermann, A., and C. Bolduan, "Radioactivity" (review), 210
- "Water, Electrolysis of" (review), 214
- Water at a temperature of 100°, action of silicon on, 259
- Booth well, composition, 9
- estimation of organic matter in, 21, 22
- purification by continuous fractional distillation, 121
- determination of carbonate of sodium necessary to precipitate the lime and magnesia for, 254
- supply, London, 52, 88, 146, 211, 242, 304
- Waters containing chlorides and bromides, estimation of organic matters in, 219
- mineral, radio-activity of, 133
- potable, in South-West Lancashire, 6
- Watson, E. R., and S. Ruhemann, contributions to knowledge of diketones, 149
- W. hints on the preparation of diagrams, 123
- quartz-tress, vertical force magnetograph, 127
- "Weights and Measures, Up to Date Table of Imperial, Russian, Indian, and Colonial" (review), 155
- Weights, atomic, report of International Committee, 68
- molecular, determining, 69
- Werner, A., and N. Goslings, carbonatopentamine cobaltic salts, 275
- "Werner's, Alfred, Theory of Carbonates and Stereochemistry of Carbocyclic Compounds" (review), 26
- Westcott, W. W., and W. H. Martindale, "Practical Pharmacopeia" (review), 167
- Wherham, W. C. D., "Treatise on the Theory of Solution" (review), 194
- Whiteley, Martha Annie, oxime of mesamide, and allied compounds, 235

- | | | | |
|---|---|---|---|
| <p>Williamson, A. W. (obituary), 237</p> <p>Winfield, H. B., G. T. Morgan, and Frances Mary Gore Mickelthwait, substitution products of <i>α</i>-tetrahydro-<i>β</i>-naphthylamine, 247</p> <p>Winkler, C., radio-activity and matter, 289</p> <p>Winterfield, G., and O. Ruff, bromides of sulphur, 287</p> <p>Wöhler, L., and A. von Dieterich, lecture experiments for demonstration of mass action, 231</p> | <p>Wolff, J., L. Maquenne, and A. Fernbach, retrogradation and coagulation of amidon, 71</p> <p>Wood, K. W., cases of interference and diffraction, 57</p> <p>Wood treated to resist fire, testing, 32, 40</p> <p>Wright, A. E., apparatus for measuring contents of human blood, 245</p> <p>Wuyts, H., and G. Cosyns, action of sulphur on organo-magnesian compounds, 227</p> | <p>"X-RAYS Simply Explained" (review), 190</p> <p>YOUNG, S., "Fractional Distillation" (review), 129</p> <p>Youtz, L. A., methods for estimation of antimony, 299</p> <p>ZINC in form of sulphide, estimation, 16</p> <p>spectrum, 251</p> <p>spark and arc, invariability of wave-lengths in, 98</p> | <p>Zinc aluminium alloys, 274</p> <p>peroxides, 95</p> <p>Zimmermann, H., "Calculating Tables" (review), 214</p> <p>P., and R. Schenk, decomposition of carbonic oxide in the blast-furnace, 180</p> <p>Zirconium and beryllium, separation, 77</p> <p>and iron, separation, 63</p> <p>behaviour toward organic bases, 15, 27</p> |
|---|---|---|---|

THE CHEMICAL NEWS, JANUARY 20, 1905.

THE
CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME XC.—1904

LONDON :

PUBLISHED AT THE OFFICE, 16, NEWCASTLE STREET, FARRINGDON ST.,
E.C.

AND SOLD BY ALL BOOKSELLERS.

MDCCCIV.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,
16, NEWCASTLE STREET, FARRINGDON STREET,
E.C.

THE CHEMICAL NEWS.

VOLUME XC.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2327.—JULY 1, 1904.

ON THE ACTION OF RADIIUM EMANATIONS ON DIAMOND.*

By Sir WILLIAM CROOKES, F.R.S.

WHEN diamonds are exposed to the impact of radiant matter in a high vacuum they phosphoresce of different hues, and assume a dark colour, becoming almost black when the bombardment is long continued (*Phil. Trans.*, 1879, Part II., p. 658, par. 625).

Some diamonds blacken in the course of a few minutes, while others require an hour or more to discolour.† This blackening is only superficial, and although no ordinary means of cleaning will remove the discolouration, it goes at once when the stone is polished with diamond powder. The fact that the black stain is not affected by ordinary oxidising reagents would seem to show that it is not due to a layer of amorphous carbon; but it might be graphite, which is much more resistant to oxidation. Becquerel has shown that graphite is converted into graphitic oxide by long digestion in a warm mixture of potassium chlorate and strong nitric acid, while diamond—even in a very finely powdered state—is absolutely unaffected by the mixture (*Ann. de Chim. et de Phys.*, [4], xix., p. 392).

Some forms of graphite dissolve in strong nitric acid; others require a mixture of highly concentrated nitric and potassium chlorate to dissolve them, and even with this intense oxidising agent some graphites resist longer than others. M. Moissan has shown that the power of resistance to nitric acid and potassium chlorate is in proportion to the temperature at which the graphite has been formed, and with reasonable certainty we can estimate this temperature by the resistance of the graphite to this reagent.

Judging from the long time required to remove the superficial darkening from diamond, the graphite is as resistant as that formed at the temperature of the electric arc.

On one occasion when I had blackened the surfaces of diamonds by molecular bombardment *in vacuo* M. Moissan was present, and took some away with him for further examination. He subsequently reported the results in the *Comptes Rendus* (vol. cxiv., No. 13). He heated the diamond to 60° in an oxidising mixture of potassium chlorate and fuming nitric acid prepared from monohydrated sulphuric acid and potassium nitrate fused and quite free from moisture. The action on the black layer is very slow. There is produced graphitic oxide, which at an increased temperature yields pyrographitic acid, easily destroyed by nitric acid. Hence the variety of carbon

which coated the diamond was graphite. The transformation of diamond into graphite requires the high temperature of the electric arc. The higher the temperature to which graphite is raised the greater is its resistance to oxidation. M. Moissan concludes that the temperature reached by the surface of the diamond in my radiant matter tubes is probably about 3600°.

The β -rays from radium having like properties to the cathode stream in a radiant matter tube, it was of interest to ascertain if they would exert a like influence on diamond. Two Bingara diamonds, A and B, weighing respectively 0.960 and 1.020 grains, were selected as near as the eye could judge of the same size and colour—very pale yellow, technically known as "off colour." Diamond A was put in a drawer far removed from radium or any radio-active body. Diamond B was kept close to a quartz tube containing about 15 m.-grms. of pure radium bromide sealed *in vacuo*. It phosphoresced brightly and continued to glow the whole time of the experiment.

After a fortnight the two diamonds were put side by side and compared. I could see no appreciable difference in colour between them. Diamond B was now replaced close to the quartz tube of radium, and they were kept in contact for six weeks. At the end of that time examination again showed scarcely any difference between the two. The one which had been near the radium might be a little the darker of the two, but the difference was too slight to enable me to speak positively.

Diamond B was now put inside a tube with radium bromide, the salt touching it on all sides, as it was thought possible that a screen of quartz might interfere with the passage of emanations which would act on the diamond. The comparison diamond was kept removed from the emanations as before. The experiment was continued for seventy-eight days, when the two diamonds were again examined. There was now a decided difference in colour between them; diamond A was of its original pale yellow "off colour," and diamond B was of a darker appearance and of a bluish green tint, with no yellow colour apparent.

It thus appears that the property which radium emanations possess of darkening transparent bodies which they impinge upon—a property very marked in the case of glass, and less with quartz—also holds good in the case of diamond.

Diamond B was now heated to 50° C. in a mixture of strongest nitric acid and potassium chlorate for ten days, the mixture being renewed each day. At the end of this time the diamond had lost its dull surface colour, and was as bright and transparent as the other stone, but its tint had changed from yellow to a pale blue-green.

The radium emanations have therefore a double action on the diamond. The β -rays (electrons) effect a superficial darkening, converting the surface into graphite in a manner similar to, but less strongly than, the more intense electrons in the cathode stream. But the alteration of the body

* A Paper read before the Royal Society, June 16th, 1904.

† At a lecture before the Royal Institution on June 11, 1897, I exposed a flat macule crystal of diamond to radiant matter bombardment before the audience for about five minutes, a strip of metal covering part of the stone. On removing the diamond from the vacuum tube and projecting its image on the screen with the electric lantern, the image of the darkening was very apparent.

colour of the stone by emanations which are obstructed by the thinnest film of solid matter, even by a piece of thin paper, is not so easy to understand. A superficial action might be expected, but not one penetrating through the whole thickness of the diamond. I believe the alteration of colour is a secondary effect; in presence of radium the diamond is extremely phosphorescent, and it continues to shine during the whole time of the experiment. This constant state of vibration in which the diamond was kept for many weeks may have caused an internal change revealing itself in a change of colour. Indeed, it is not difficult to suppose that a chemical as well as a physical action may result. If the yellow colour is due to iron in the ferric state a reduction to the ferrous state would quite account for the change of colour to a pale blue-green.

This alteration of colour may be of commercial importance. If "off colour" stones can be lightened their value will increase, while if the prolonged action of radium is to communicate to them a decided colour they would be worth much more as "fancy" stones.

[Added June 16, 1904.—After the ten days' heating in the above acid mixture the two diamonds were put together in a glass tube and carried about for twenty-five days, sometimes loose and sometimes in the tube. They were then laid near together on a sensitive film in total darkness for twenty-four hours. On developing, diamond B had impressed a strong image on the film, but only a very faint mark could be seen where the other diamond had been.

The experiment was then repeated for confirmation, allowing the diamonds to remain in contact with the sensitive surface for only five hours. On development, a good image of diamond B was seen, but not so black as in the former case.

The fact that diamond B was strongly radio-active after it had been away from the radium for thirty-five days—for ten of which it was being heated in a mixture powerful enough to dissolve off its outer skin of graphite—seems to me proof that radio-activity is by no means a simple phenomenon. It not merely consists in the adhesion of electrons or emanations given off by radium to the surface of an adjacent body, but the property is one involving deep-seated layers below the surface, and, like the alteration of tint, is probably closely connected with the intense phosphorescence the stone had been experiencing during its seventy-eight days' burial in radium bromide].

The British Journal of Photography.—The proprietors of this valuable journal have recently published a "Jubilee Number" to mark the fiftieth year of its publication, though it has not always been known by the title it now bears. It was first started on January the 14th, 1854, as the *Liverpool Photographic Journal*, and after going through many evolutionary changes it assumed its permanent title of *The British Journal of Photography* on January 1st, 1860, at which time it was in the able hands of Mr. Henry Greenwood, who retained control until his death in 1884. This "Jubilee Number" contains thirty special articles on the most popular and prominent phases of modern photography, written by competent specialists, besides an illustrated history of the journal since its foundation. In this history we find a list of the editors, among whom are many well-known men who have since made their mark in the world of science. Among these we may mention James Alexander Forrest, 1854-1856; George Shadbolt, 1857-1864; George Dawson, Samuel Highley, Sir William Crookes, James Martin, John Traill Taylor, W. R. Bolton, and last but not least, Thomas Bedding, who at present fills the editorial chair in such an able manner. Such an event as the publication of this "Jubilee Number" is unique in the annals of photography, and marks an important epoch in the science. We heartily congratulate our contemporary on the success it has already achieved, and trust that it will continue to flourish in the future as it has done in the past.

TECHNICAL RESEARCH AND THE COLLEGE SYSTEM.

II.

By W. P. DREAPER, F.I.C., &c.

IN connection with my recent proposals for a systematic scheme of technical research in our scientific colleges, the question naturally presents itself, Is the training given to the students of such a nature that it will enable them to undertake the experimental work necessary for such a scheme in an intelligent way? If they are not capable of entering in their last year upon any suggested research, then it follows that they are equally incapable of entering the industrial world as anything more than routine men.

Some time ago, Prof. H. E. Armstrong complained rather bitterly that the material sent up from the schools was of an inferior nature, and that this was a very serious difficulty in the way of technical training. No one outside the schoolmaster circle will seriously deny the truth of this statement. There can be no doubt that the students sent up from the schools are seriously deficient in the power of thinking for themselves. As possible curates their qualifications may be supreme. As thinkers and workers combined their preliminary training is, as has been stated, a national scandal and in itself enough to throw doubt upon our whole scholastic system with its pedantry and empiricism.

Important as this question may be, I only wish to mention it in passing as playing some part in the subject before us. My object is to draw attention to the importance of giving a more human element to the teaching of the exact sciences by connecting the facts with the processes by which they were established, and these in their turn with the men who worked them out; for is not the ultimate place for the technical student in the experiment world? He must be trained on such lines that he will first of all be taught to think for himself. In order that this may be the prime idea in his educational course, it is contended that the whole character of his training should be more personal in its nature than it is to-day.

If the text-books of to-day are examined it will be found in the majority of cases that they are calculated to fill the student's mind with a set of relatively immaterial facts. There seems to be a tendency in the more advanced ones, perhaps on account of examination requirements, to stuff them with secondary matter which properly belongs to some standard book of reference, and to lose sight of the importance of keeping main ideas absolutely to the front as connecting chains of thought.

The modern text-book tends to become more diffused in its nature. The authors seem unable to carry the burden of their accumulated facts with interest to themselves or instruction to their readers. This is unfortunately liable to stereotype the course of a college by limiting it to the lines and ideas of a certain collector of facts, be he one of the college staff or not.

The whole routine of the college should within necessary limits be of as personal nature as possible, in order that the student may feel—may I say it?—at home in his work, or rather in the work of the greatest experimenters of the age.

May I give a very simple instance of what I mean, taking the preparation of oxygen as an example? Here Priestley's name and influence should reign supreme. The lecture should start with an account of his experience with the then unknown. Step by step his work should be followed from the personal side as well as the experimental. The influence of the man experimenting should be present. His actions, which will be of a similar nature to those of the student in his subsequent life's work, should occupy a prominent position in the record-impression on the student's mind.

It is surely not too much to say that all the knowledge which is available is of this personal nature. Here a touch from one hand, and there a gentle moulding from another.

Systems and lines of thought must have their day. They will merge into the light of our more extended experience, but a student's knowledge will never become useless or quite out of date if it is based on the personal experience of those men who have contributed their quota to the discoveries of the age. It will be easier for the worker to change his ideas, if needs be, if his mind is imbued by the processes by which those ideas were formed; with the enthusiasm this will create, he will be better able to keep abreast of the times.

After all, our knowledge is nothing more than the collected experience of those who have stepped in advance of the crowd. Our knowledge is so strictly personal that it may not extend outside ourselves. It may be ridiculously trivial when compared with the absolute. Be this as it may, the personal side of the question is sacred to the memory of those who have extended our lines of thought, and the students of to-day will be the better workers of to-morrow if this side is uppermost instead of being suppressed under a load of bare facts.

This training would surround the student, even in his early days, with an influence that would lead him to wish to do something more than mix solutions in a test-tube. He would somehow get hold of the idea that here Priestley stepped in, did so and so, and obtained such a result; or at this point Darwin suffused the whole of biology with his thought. Evolution is one of the few cases where perhaps the influence of the man is supreme. To this may be attributed the extraordinary advance in this subject since the publication of his work; or we may at least divide it equally with the attraction of the subject itself.

When the student reaches his "work period" with thoughts like these, he will drive through many difficulties. Is it too much to say that the nation that first learns this lesson will be the nation to lead? The suppression of the personal in science is not an advantage, it is a serious defect.

To pass on to the professor's influence. In the majority of cases this is of too impersonal a nature. The students freeze in the light of a Polar star. Many English students know as little about their professors as a lay reader about his bishop. This should not be. The old cry for "facts" must give way to the more important cry of "personality."

It is clear from the confession of its students that that wonderful school of which Liebig was the master derived a great deal of its power from the personality of its leader. Yet many of our professors never indicate by word or deed that they have ever been students, any more than a certain famous minister in fiction ever indicated in the pulpit that he had lived. Yet every student's eye is rivetted on his instructor, but in many cases the latter has burnt his boats behind him, and the students stand on the other side of the water. A well-known manufacturer and chemist recently said at Burlington House, "Save us from the professors," but the student's only wish is to know what kind of a man he really is and the secret of his success.

Yet all the social considerations are against this in this country, and it seems to be an unwritten law that a lecturer shall say as little as possible about his own work at the lecture table.

In after years our thoughts undoubtedly turn more from the personal to either facts or things. If to the former, our life's work is already nearly over.

This great personal influence, important as it is, is lost sight of in many of our scientific colleges and departments, but it is this factor that will enable students to obtain the "hang" of any research they may have to take part in under any such scheme as I outlined in my previous article.

In order that the future workers may have the power to grapple with the problems before them, they must be acquainted with the difficulties and successes of others, working as they must work. This side of their training is often conspicuous by its absence. The successes of the past are crystallised to-day into dry facts; the difficulties not considered. How then shall the young workers meet

their own difficulties, and not be discouraged? For out of the difficulties of the technical worker must chiefly spring his original work; and the student of to-day is the technical worker of to-morrow. With him may rest the future of our industrial position.

ON THE CHARACTERISATION OF LEAD:

AN ANSWER TO HERR CLEMENS WINKLER.

By K. A. HOIMANN.

In the article (*Berichte*, 1904, xxxvii., 1657) on "Radio-activity and Matter," which has recently appeared, Herr Clemens Winkler casts doubts on the accuracy of the equivalent weight determinations which I performed with the active lead sulphate obtained from pitchblende, because my preparations were dried only at 400° to 420°, and "experience has proved that at such a low temperature it is not possible" to expel completely the free sulphuric acid which adheres to it, so that thus the strikingly high percentage of sulphuric acid (41.35 per cent instead of 31.71 per cent for ordinary lead sulphate), which I found, cannot forthwith be accepted as indicating the presence of a metal of lower equivalent weight. In answer to this I should like to say that, according to my control experiments previously performed, pure ordinary lead nitrate on evaporation with a moderate excess of pure sulphuric acid, even at about 300°, gives the theoretical quantity of sulphate, and thus retains no free acid, but is of the normal composition. But because the objection mentioned above was raised by a chemist who is an authority in the region of analytical chemistry, and because the point in question is of the greatest importance for the gravimetric determination of lead, I repeated my experiments, and thus confirmed my earlier results.

I used lead nitrate which was prepared from electrolytically separated lead dioxide, and had been purified by repeated re-crystallisation.

The separate specimens were dried *in vacuo* (cf. Leo Backeland, *Fourm. Amer. Chem. Soc.*, xxvi., 391), and after heating to 100° for one hour their weight was constant. They were then dissolved in water, and converted into sulphate by evaporation with a moderate excess of pure dilute sulphuric acid at 270°, and the sulphate was heated (1) for 1.5 hours at 320°, (2) then for five hours at 355°, (3) then for 1.5 hours at 390°, and (4) for ten minutes at incipient red heat.

- i. 0.2564 grm. nitrate should theoretically* give 0.2347 grm. sulphate. The weighings gave—(1) 0.2349, (2) 0.2346, (3) 0.2344, (4) 0.2346 grm. sulphate.
- ii. 0.5556 grm. nitrate should theoretically give 0.5086 grm. sulphate. The weighings gave—(1) 0.5091, (2) 0.5085, (3) 0.5084, (4) 0.5087 grm. sulphate.
- iii. 0.2655 grm. nitrate should theoretically give 0.2430 grm. sulphate. The weighings gave—(1) 0.2433, (2) 0.2432, (3) 0.2431, (4) 0.2431 grm. sulphate.
- iv. 0.1926 grm. nitrate should theoretically give 0.1763 grm. sulphate. The weighings gave—(1) 0.1768, (2) 0.1760, (3) 0.1758, (4) 0.1762 grm. sulphate.

Hence it follows that on evaporation of pure lead nitrate with excess of sulphuric acid, even at temperatures below 400°, it is completely converted into normal sulphate. Thus the excess of sulphuric acid found according to my analysis in the radio-lead sulphate dried at 400° to 420° cannot be due to adhering free acid, but proves the presence of a substance different from ordinary lead, and I hope shortly to report definitely on its qualitative and quantitative behaviour.—*Berichte*, 1904, xxxvii., 2197.

* O=16 according to the International Atomic Weight Table

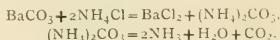
THE
DECOMPOSITION OF THE ALKALINE-EARTHY
CARBONATES BY CHLORIDE OF
AMMONIUM IN THE PRESENCE OF WATER.

By H. CANTONI and G. GOGUELIA.

A. *Action of Chloride of Ammonium on Carbonate of Barium in the presence of Water at Boiling-point.*

WHEN we add powdered carbonate of barium to a solution of chloride of ammonium of medium concentration, and heat to boiling for a certain time, a part or the whole of the carbonate of barium—according to the conditions under which the operation is carried out—passes into solution in the state of chloride of barium.

The filtered solution, which should contain only chloride of barium, and, according to H. Schreib, carbonate of ammonium, does not become cloudy on cooling. Further, we have not detected any traces of fixed carbonic anhydride. All the carbonic acid escapes according to the following equations:—



To make quite certain that the whole of the carbonic acid displaced from the carbonate of barium escapes, and does not unite with the ammonia in any proportion, we have estimated the CO_2 given off during the decomposition.

The carbonic acid found corresponds exactly with the amount of carbonate of barium passing into the state of soluble chloride.

The flask in which the double decomposition was made is fitted with a vertical condenser, so that the concentration of the solution of chloride of ammonium may be constant during the whole time of the operation. At the top of the condenser is fixed a washing bulb containing sulphuric acid. Following this bulb, which serves to retain the ammonia, are U-tubes containing chloride of calcium to dry the gas. Finally, a Liebig potash tube containing a solution of caustic potash (1 part of KOH, 2 parts of water) serves to retain quantitatively the carbonic anhydride.

A current of air, previously freed from its carbonic acid, circulates through the apparatus and drives all the CO_2 into the tube arranged for its estimation.

We have made several trials to determine the conditions of this decomposition by varying both the time of boiling and the concentration of the solution of chloride of ammonium.

H. Schreib, in a paper published in 1889, determined the decomposition of carbonate of lime by chloride of ammonium, but these experiments were not carried out on solutions of varying concentrations of NH_4Cl .

By taking $\frac{1}{10}$ th of a gram-molecule of carbonate of barium, and $\frac{2}{5}$ th of a gram-molecule of chloride of ammonium dissolved in 500 c.c. of water, and heating to boiling for one hour thirty minutes, we obtained from several gravimetric estimations of the filtered solution 1.5455 grms. of carbonate of barium which had passed into the state of soluble chloride.

It will be seen that instead of having the quantity of carbonate of barium solubilised, corresponding to the chloride of ammonium used, we have only $\frac{1}{10}$ th.

We have repeated this experiment under the same conditions, but increasing the time of boiling. When boiled for twenty-four hours the amount of BaCO_3 decomposed was 2.1375 grms.; that is, $\frac{3}{10}$ ths of the amount equivalent to the chloride of ammonium used.

In another experiment, we heated to boiling for forty-eight hours, and we found 2.4732 grms. of BaCO_3 decomposed; that is, half the amount of carbonate of barium corresponding to that of the chloride of ammonium used.

In another series of experiments we increased successively the concentration of the solution of chloride of ammonium. With 42.8 grms. of NH_4Cl , or sixteen times the amount

previously used, and after heating to boiling for one hour thirty minutes, 7.946 grms. of BaCO_3 were decomposed. The constant quantity of carbonate of barium in these two series of experiments was 9.87 grms.

B. *Determination of the Time necessary for the complete Decomposition of the Carbonate of Barium.*

To get an estimate of the time necessary for the complete transformation of the carbonate into chloride by the prolonged action of chloride of ammonium in the presence of water, and at boiling temperature, we made two series of experiments; one with different quantities of chloride of ammonium in a constant quantity of water in the presence of an invariable weight of carbonate of barium, and at boiling temperature; the other with 1 gram-molecule of BaCO_3 and twice the amount of NH_4Cl in 500 c.c. of water, boiling for different times. We give the results of these different experiments.

When we heat powdered carbonate of barium to boiling with a solution of chloride of ammonium of known strength for a given time in a round bottomed flask of Jena glass of 100 c.c. capacity, fitted with a vertical condenser, all the carbonate of barium present is decomposed, and changed into the state of chloride of barium. The liquid in the flask has a milky appearance at the commencement of the operation on account of the presence of the insoluble carbonate of barium; it becomes perfectly limpid, and does not contain a trace of BaCO_3 after having been boiled for a suitable time.

197.4 grms. of chloride of ammonium in 500 c.c. of water decomposed 9.87 grms. of carbonate of barium almost instantly; at the moment of boiling the liquor became perfectly limpid.

With the molecular weight of NH_4Cl , that is 53.5 grms. in 500 c.c. of water, three quarters of an hour were required to decompose 9.87 grms. of barium.

We were obliged to heat for sixteen hours to decompose 9.87 grms. of BaCO_3 with a solution of 21.4 grms. of NH_4Cl in 500 c.c. of water. These figures suffice to show how BaCO_3 is decomposed by solutions of NH_4Cl at boiling temperature. All these experiments were made with the same carbonate of barium, pulverised to the same grade. H. Schreib has shown distinctly the different actions of chloride of ammonium on the different carbonates of lime, and also the importance the state of the carbonate used has on these determinations.

C. *Action of Chloride of Ammonium on the Carbonates of Barium, Calcium, and Strontium in the presence of Water at the ordinary Temperature.*

Carbonate of Barium.—When we add powdered carbonate of barium to a solution of chloride of ammonium of medium strength at the ordinary temperature, we observe that after a fairly long time a portion of the carbonate of barium is decomposed.

We have made several experiments at the ordinary temperature during a similar time, but with solutions of chloride of ammonium of different mean strengths.

When we used a solution of 1 gram-molecule strength of chloride of ammonium, that is 53.5 grms. in 1000 c.c. of water, and an excess of powdered carbonate of barium, and kept it for ninety-eight days at the ordinary temperature, say 15°, 0.919325 gram. of BaCO_3 was decomposed.

When operating under exactly the same conditions as regards time and temperature, but with a 10 per cent solution of chloride of ammonium, 1.255651 grms. of BaCO_3 were decomposed.

We found that 1.5 grms. of BaCO_3 were decomposed when operating in the same way, but with a solution of chloride of ammonium containing 200 grms. of NH_4Cl per litre; that is 20 per cent.

Carbonate of Calcium.—The results obtained with carbonate of calcium are different from those obtained with carbonate of barium; they are much lower.

By operating with a 5.35 per cent solution of NH_4Cl for

ninety-eight days at the ordinary temperature (15°) in the presence of an excess of CaCO_3 , 0.42252 grm. was transferred to CaCl_2 .

With a 10 per cent solution of chloride of ammonium, we obtained 0.60144 grm. and 0.6480 grm. with a 20 per cent solution, the time and temperature being constant.

Carbonate of Strontium.—Of the three alkaline earthy carbonates, carbonate of strontium is the most difficult to decompose by means of aqueous solutions of chloride of ammonium.

After leaving a 5.35 per cent solution of NH_4Cl for ninety-eight days in the presence of an excess of carbonate of strontium at the ordinary temperature (15°), 0.17944 grm. of the carbonate was decomposed.

By working under exactly the same conditions, but with a 10 per cent solution of chloride of ammonium, 0.25936 grm. was decomposed.

With a 20 per cent solution of chloride of ammonium, we found 0.35808 grm. of SrCO_3 was decomposed.

All the experiments at the ordinary temperature were carried out in specially made hermetically sealed vessels. The temperature was kept constant within the closest limits possible for ninety-eight days.

In the following table we give the results obtained in the cold with the different carbonates so that they may be compared easily.

Table showing the Decomposition of the Alkaline-earthly Carbonates by Cold Aqueous Solutions of NH_4Cl .

Per cent of NH_4Cl solution.	Temperature.	Time in days.	Grams. of carbonate decomposed.		
			BaCO_3 .	CaCO_3 .	SrCO_3 .
5.35	15°	98	0.91745	0.42252	0.17944
5.35	15°	98	0.92120	0.42436	0.17830
10	15°	98	1.255122	0.60144	0.25936
10	15°	98	1.256180	0.61732	0.2606
20	15°	98	1.50000	0.64800	0.35808
20	15°	98	1.49640	0.64320	0.35890

The above experiments lasted from January 27 to May 4, 1903.

In his paper in 1889, H. Schreib declared that carbonate of lime was not decomposed by chloride of ammonium in cold aqueous solution. Doubtless he did not prolong his experiments sufficiently, as we see that with a 20 per cent solution of NH_4Cl , for example, we have 0.648 grm. of CaCO_3 decomposed. (An excess of CaCO_3 in 1 litre of a 20 per cent solution of NH_4Cl at 15° for ninety-eight days).

Our experiments show further the difficulty there is to free the alkalis from the alkaline-earthly metals in the analysis of silicates. (Estimation of the alkalis). After having decomposed the silicate by HFl and H_2SO_4 , we precipitate the sulphuric acid with BaCl_2 , then treat with NH_3 to precipitate the iron, alumina, and part of the magnesia; then with carbonate of ammonium we precipitate the lime from the silicate and the excess of BaCl_2 . Now we have BaCO_3 , CaCO_3 , NH_4Cl , KCl , and NaCl left; by slightly raising the temperature a large part of the carbonates are made soluble. It is for this reason that great care and several successive calcinations are needed to free the alkalis from the alkaline-earthly metals.

The attack of these different carbonates by the alkaline chlorides leads us to expect that this phenomenon of decomposition ought to be repeated with the oxalates, phosphates, sulphates, &c., of the alkaline earths.

Finally, it may be observed that the attack of carbonate of strontium by chloride of ammonium, and probably by other salts as well, causes the estimation of strontium as carbonate to be inexact, except under exceptional circumstances; therefore, when we have to estimate the alkaline-earthly metals in a solution containing saline substances, and especially alkaline chlorides, it would be more prudent to adopt a volumetric method, or some indirect process.—*Bull. Soc. Chim., Series 3, vol. xxxi., No. 6.*

ON ALUMINIUM POWDER AND THE OXIDATION OF ALUMINIUM.

By E. KOHN-ABREST.

ALUMINIUM does not seem to have been studied sufficiently up to the present time from the point of view of its chemical affinities.

It is certain that under ordinary circumstances pure aluminium does not undergo any appreciable changes. It is, however, the no less true that the oxidability of this metal is extreme.

An old experiment of Jahn's (*Berichte*, 1875) shows that contact with a trace of mercury is sufficient to cause an abundant and magnificent efflorescence, due to the oxidation of the aluminium. Le Bon has examined this reaction in greater detail, and we will return to it later on.

Deville, Dumas, Ditte, Moissan, Riche, Hugouencq, Balland, and numerous other chemists having examined this metal, have observed the ease with which it becomes oxidised in the presence of small quantities of iron and silicon. These are, in fact, the principal impurities of aluminium. Actual nodules of alumina are formed under certain conditions at the places where the metal is no longer homogeneous.

The progress of the industry has enabled me to prepare metals sufficiently pure for the attack caused by water, chlorides, the alkalis, and various foods to be relatively weak.

But if we examine the chemical affinities of the relatively pure metals, from the theoretical point of view, when they are in the form of powder, the refractibility of the aluminium is far from remaining the same.

Aluminium Powder.

Aluminium powder is prepared commercially by submitting the hot pure metal to certain mechanical treatment. Most of these powders contain a variable proportion of fatty matters.

When we treat aluminium powder, freed from fat by means of ether, with hydrochloric acid it is almost completely dissolved. The insoluble residue, according to some authors, consists of carbon, silicon, and traces of aluminium, and does not exceed 0.6 per cent of the total mass.

The estimation of the aluminium in hydrochloric solution, by precipitation with ammonia, does not give more than 94 per cent of aluminium and iron together. The difference, at least to a great extent, is due to oxygen. We have proved this in several different manners.

Methods for the Rapid Estimation of Metallic Aluminium in the Form of Powder.

1. *By the Weight of Hydrogen given off during the Attack by Hydrochloric Acid.*—In a flask of 500 c.c. capacity, fitted with a stopper carrying a funnel with a tap, and communicating on the one hand with an apparatus for making pure carbonic acid gas, and on the other with drying tubes of sulphuric acid in pumice stone, and a tube containing oxide of copper heated to dull red, we place 0.5 to 1.0 grm. of the weighed substance wrapped up in a cigarette paper.

Add a little water, and close the apparatus. After having washed out the air by means of a current of carbonic acid, there only remains to proceed with the attack with hydrochloric acid of one-third strength poured in through the funnel. During the attack, which is made very rapid by heating on the water-bath, the current of carbonic acid is stopped as much as possible; it also serves to wash out the hydrogen at the end of the operation.

The hydrogen reduces the oxide of copper, and the water formed is collected in a tared sulphuric acid and pumice stone tube. Taking the atomic weight of aluminium at 27, we find that 1 grm. of aluminium gives 1 grm. of water. By means of a three-way cock placed in the circuit we can re-oxidise the copper in air, and dry the tube if necessary.

The Tared Tube.—The tube should be tared while full of carbonic acid and weighed with the two ends closed. A second pumice and acid tube should be placed in series to prevent the access of atmospheric moisture to the tared tube. One particular sample gave us in four operations, 91.0, 91.28, 91.3, and 91.67 per cent. When once this apparatus is set up rapid results can be obtained.

2. *Estimation by the Reduction of Ferric Sulphate.*—A. Wahl has described a beautiful and rapid method for the estimation of zinc powder, based on the reduction of ferric sulphate by this powder. We have endeavoured to apply the principle of this method to aluminium. The reaction should be as follows: $3\text{Fe}_2(\text{SO}_4)_3 + 2\text{Al} = \text{Al}_2(\text{SO}_4)_3 + 6\text{FeSO}_4$, from which we find that one part of iron corresponds to 0.1607 of aluminium.

Application.—Into a narrow necked flask we weigh out 5 decigrams of the metallic powder. After the addition of 20 grms., that is to say, a large excess of ferric sulphate without action on permanganate, we add about 50 c.c. of water. The flask is closed by means of a stopper having two tubes suitably arranged for a current of carbonic acid to bubble through the mass during the whole of the operation. As the reduction only takes place when hot, the flask is placed on the water-bath. At the end of an hour, the aluminium powder has disappeared, and the ferric sulphate is completely dissolved. After cooling rapidly in the current of carbonic acid, the solution is completed and made acid by the addition of 20 c.c. of concentrated sulphuric acid. There only remains to dilute to 250 c.c., and to estimate the ferrous salt on a known portion of the liquid by means of a titrated solution of permanganate of potassium.

With a solution of permanganate containing 3.163 grms. per litre, for example, 1 c.c. corresponds to 0.00062968 of aluminium. It is better, however, to work with more concentrated solutions of permanganate. Our experiments have given us a mean of 91.4 per cent of aluminium, a result which concords with the other method. We have already stated that impurities are present in the sample; these are particularly silicon and iron. It is possible to make certain that it is only the iron which is the cause of error. We may, in fact, assume that it exists in the metallic state, and consequently gives rise to a disengagement of hydrogen during the first process of the estimation, and to a reduction of permanganate in the second. It is quite otherwise in so far as the silicon is concerned in aluminium powder. Some observations are here necessary on this subject.

The state in which the Silicon exists in Powdered Aluminium.

Silicon is a body which is capable of existing in three separate states: the amorphous, the crystalline, and the graphitoid. The amorphous form, according to Deville (*Ann. Chim. Phys.*, [3], vol. xlix., p. 68), is oxidisable in warm air, and is only soluble in hydrofluoric acid. The two other very stable forms are equally unattacked by any other acids than the mixture of hydrofluoric and nitric acids (Deville).

In the aluminium powder treated with hot dilute hydrochloric acid we observe a very slight insoluble residue. It is quite possible that this residue may contain graphitoid silicon. We know that by electrolysis the sodico-aluminic chloride Sainte-Claire Deville observed the existence of graphitoid silicon in the metal. This silicon comes from the electrodes of siliceous carbon, which, on contact with the hot aluminium, introduces silicon into the aluminium.

But this small amount of graphitoid silicon insoluble in acids does not represent the whole of the silicon present. In fact, when we evaporate the filtered hydrochloric solution to dryness, and leave the residue for a sufficient time in the oven at about 170° in a platinum crucible, the silica is rendered insoluble. In our experiments this amount was equal to 0.608 of silicon. This is quite sufficient to show that there is silicon in the aluminium powder. We may remark here that Deville states that silicised aluminium

becomes inflamed when heated, and burns with remarkable brilliancy, with the formation of silicon and silicate of alumina. To sum up, the silicon present in aluminium powder is only to a slight extent in the form of insoluble silicon, but principally as silica. These observations should be borne in mind in making the analyses.

Direct Detection of Alumina in Aluminium Powder.

The difference between the percentage of aluminium precipitated and estimated in the form of alumina in a liquid free from silica, and the percentage of the metal obtained by one of the two processes, gives, within the errors due to iron, sodium, &c., the quantity of pure oxidised aluminium which is present in the powder. The following is one of these analyses:—

	Per cent.
Aluminium and iron	91.20
Alumina	5.80
Silica	1.30
Graphitic and insoluble silicon (not estimated) ..	0.40
Carbon	0.23
Moisture and loss (by difference)	1.07
Total	100.00

But we have endeavoured to apply direct methods; in other words, to separate the alumina and the silica from the remainder of the powder, and for this purpose we have undertaken various experiments.

Before dealing with this point let us observe that M. Moissan has described (*Comptes Rendus*, vol. cxxi., p. 794) a method for the estimation of the original alumina. He passed a current of chlorine over the substance placed in a tared boat, and heated to reddish-white heat in a porcelain tube. The metallic aluminium is volatilised in the state of chloride, and the fixed residue when weighed gives the alumina.

We have endeavoured to make the alumina insoluble by submitting the aluminium powder to a prolonged heating above 200°. It appeared to us advisable to first examine methodically the oxidation of this substance at different temperatures.

Wohler observed (*Ann. der Chem. u. Pharm.*, vol. xciii., p. 249) that aluminium heated in oxygen burned vigorously. We have repeated this experiment with our powder, and we found that at a bright red heat it takes fire and burns with brilliancy, giving rise to the formation of a mass of oxide, covering globules of the fused unoxidised metal; the proportion of metal oxidised under these conditions is about 50 per cent. However, the fact is well known, and has been observed on many occasions. The same action does not take place when the metal is in strips. M. Matignon in his work on aluminothermics (*Revue Generale des Sciences*, November 15, 1903) shows that in this case the metal melts under a very thin layer of alumina, which protects it from further oxidation; we have also observed this fact.

Now what happens to aluminium powder heated in air to temperatures below its fusion-point? Is it unchanged to the point generally thought to be the case with aluminium, even in the presence of certain quantities of iron and silicon? This does not appear to be quite the case according to our experiments. The following are a few of the results we obtained:—

Aluminium Powder kept in the Oven at 100° for a Week.—No increase in weight.

Aluminium Powder kept in the Oven at about 175° for a Week.—There were slight but variable increases in weight according to the experiment; in one there was no increase; thus the results are uncertain.

Under these circumstances, as we have been able to prove, it is only possible to insolubilise alumina with great difficulty. We have succeeded partially by leaving a sealed tube containing the metallic powder and another tube with chloride of calcium in the oven for a long time. The process is not practicable, however.

Aluminium Powder heated in the Air to about 400.— Very rapid oxidation. A method for its estimation can be devised from this.

Experiment.—Heat the aluminium powder in an ordinary current of air for twelve hours in a tared boat.

Weight of substance... 0.3217 grm.
Increase due to heating in air... 0.0263 "

If we attribute this increase to oxygen, it represents 0.058 grm. of alumina. If we take up the aluminium powder with hydrochloric acid, after weighing, an abundant residue remains consisting of alumina and insolubilised silica. This residue in this experiment was washed, dried, and weighed; after calcination it gave 0.814 of alumina and silica together.

The difference between the total alumina and the alumina due to oxidation is the original alumina (and silica) in the material. In this case it was 7.7 per cent. So that the analysis of the powder gives:—

Metallic Al and Fe... 91.2
Silica and alumina... 7.7

This insolubilisation of the alumina can also be brought about in hydrogen under certain circumstances. We shall return to this point in another part of our research.

Oxidation of Aluminium Powder in the Cold.—The work done since Wöhler and Deville, establishes the corrosive action of a number of compounds on impure aluminium. We will add a few new observations on this subject.

It is known that when we put aluminium in contact with a solution of chloride of aluminium a sub-chloride is formed. In the same manner Berzelius observed the existence of a subsulphate by putting hydrated alumina and sulphate of alumina together.

We are of the opinion that under certain conditions, such as follows, a sub-oxide of aluminium is formed; aluminium may react directly on hydrated alumina in the following manner:—

1. When, by means of ammoniacal precipitation, we obtain alumina, and when we add powdered aluminium to the liquid thus containing dilute ammonia and ammonia chloride, after a little time we observe that the metal completely disappears in the gelatinous mass. The latter becomes perfectly white. When dried in vacuo after filtration and washing, the powder obtained does not show a single metallic particle when examined under the microscope.

2. Powdered aluminium put in contact with hydrate of alumina, in water, only shows this action to a partial extent after twenty-four hours.

3. Powdered aluminium in contact with alumina in a distinctly ammoniacal solution, but not containing a sensible amount of hydrochlorate of ammonia, produces the same phenomenon as described above in par. 1.

4. Powdered aluminium in the presence of hydrated alumina, in a dilute solution of hydrochlorate of ammonia, without free ammonia, only undergoes partial transformation in the same interval of time.

5. Aluminium powder placed in ammoniacal water, without hydrated alumina, is only slightly attacked.

6. Finally, powdered aluminium placed in a neutral solution of hydrochlorate of ammonia only undergoes slow and partial transformation.

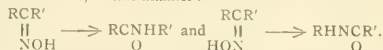
It results from the above observations, that aluminium powder is oxidised on contact with alumina; this oxidation is particularly rapid and is also complete in ammoniacal liquor. We are continuing this research.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 5.

Society of Arts Silver Medal.—The Council of the Society of Arts have awarded Mr. Thomas Tyrer the Society's Silver Medal for his paper on "The Need of Duty-Free Spirit for Industrial Purposes," and the presentation of the Medal will take place at the opening meeting of the Society's session in November next.

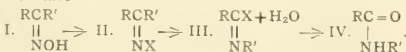
THE BECKMANN REARRANGEMENT: TRANSFORMATION OF ACETOPHENOXIME INTO ACETANILIDE AND ITS VELOCITY.*

By Prof. C. A. LOBRY DE BRUYN and C. H. SLUITER.

AMONG the many intramolecular rearrangements known in organic chemistry, the one associated with the name of Beckmann belongs to one of the most important series on account of the extent of its region and its scientific significance. As is well known, it consists in the transformation of the oximes, under the influence of a certain number of reagents, into the isomeric acid amides; for instance, $R_2C=NOH \rightarrow RCONHR$. Its extent is obvious if we remember that all ketones and aldehydes are capable of yielding oximes, and that a large number of these, particularly of the ketoximes, can undergo the re-arrangement. Its scientific importance is chiefly due to the fact that its application to the stereoisomeric ketoximes has been the means of determining the configuration of those stereoisomers, in this manner:—



The rearrangement generally takes place under the influence of different reagents, such as sulphuric acid, hydrochloric acid, phosphorus pentachloride and oxide, acyl chlorides, acetic acid with its anhydride and HCl, zinc chloride, alkalis. As these substances are always applied in relatively large quantities, it is thought most probable that the actual rearrangement nearly always relates to intermediate products, additive compounds or derivatives of the oximes, which occasionally have been separated.† These intermediate products then contain a negative group (or the group OK) attached to the nitrogen which changes place with the C-combined alkyl- or aryl-group. On subsequent treatment with water the amide is generated. We then have—

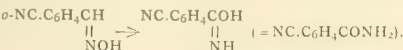


That hydroxyl itself can assume the function of the group X which changes place with R' is shown by the interesting observations of Werner and Buss (*Ber.*, 1894, xxvii., 2198), Werner and Skiba (*Ber.*, 1899, xxxii., 1654), Posner (*Ber.*, 1897, xxx., 1693), and Auwers and Czerny (*Ber.*, 1898, xxxi., 2692), who have noticed some cases of the Beckmann rearrangement in the absence of any reagent. Dibenz-

hydroxamic acid, $C_6H_5COCOC_6H_5$, obtained from chloro-

benzhydroxamic acid, $C_6H_5C.Cl$, by means of silver

benzoate, melts at 95°; according to Werner and Buss it changes after some days spontaneously into its isomer, $C_6H_5CO.NHOCOC_6H_5$, m. p. 161°; on heating this takes place more rapidly. Posner observed that o-cyanobenzaldoxime changes into its isomer when simply heated above its melting-point; it first melts at 175°, then solidifies, and finally melts again at 203°. Here we consequently have the direct conversion—



Finally, Auwers and Czerny have found that o-oxo-m-methylbenzophenonoxime, $HO.H_3CC_6H_3C-C_6H_5$, partly

* Koninklijke Akademie van Wetenschappen te Amsterdam. Reported in *Proceedings of the Meeting of Saturday, April 23, 1904*.
† Beckmann, for instance (*Ber.*, viii., 988), obtained $C_6H_5COC_6H_5$ from $(C_6H_5)_2C=NOH$ and PCl_5 . It is very probable that $(C_6H_5)_2C=NC$ is formed first as an intermediate product.

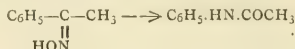
undergoes the Beckmann rearrangement when submitted to distillation.

These observations from Werner and his pupils, of Posner, and of Auwers and Czerny are of fundamental importance for the understanding of the mechanism of the Beckmann rearrangement. They prove that this important transformation is most decidedly a real intramolecular rearrangement, which may occur in some cases with the oxime, but in the majority of cases with derivatives in which, instead of the OH-group, another negative group or a halogen has been attached to the nitrogen. In that case the change from II. into III. represents the actual rearrangement.

Auwers and Czerny have already pointed out that the above rearrangement caused by distillation deserves the closest attention. They are of opinion that this observation leads to the view that the Beckmann rearrangement is a catalytic process which is in accord with Beckmann's own ideas. But is it permissible to speak of a catalytic process when the catalyst is wanting? And do not Auwers and Czerny withdraw their own statement when they say that "es sich vielmehr handelt um die directe Ueberführung eines weniger stabilen System in ein stabileres?"

The Beckmann rearrangement has not, up to the present, been subjected to a dynamical investigation. Such a study is not rendered less desirable or less important by the fact that, as a rule, the rearrangement of the intermediate product and not that of the oximes themselves will be investigated.

The oxime which has been studied in the first place is acetophenoneoxime, of which only one form is known, and which quantitatively passes into acetanilide. Its configuration is therefore—



The rearrangement, which Beckmann found to take place under the influence of concentrated sulphuric acid, was studied in the first place. Before starting it was necessary to work out an analytical method allowing the quantitative determination of the resulting anilide in the presence of the unchanged oxime. After several preliminary experiments it was found that the anilide formed on adding water was completely hydrolysed by boiling for a few hours, and that the acetic acid could then be distilled off and titrated; the excess of oxime did not interfere. We have in consequence determined the velocity with which the anilide was formed. In carrying out the experiments 2.5 grms. of the oxime were dissolved in 50 or 100 c.c. of sulphuric acid, previously heated to the temperature at which the experiment was made (65° or 65°), and at definite periods a certain quantity was pipetted off from the bottle (which was placed in a thermostat) and analysed.

The reaction proved to be one of the first order, the velocity constant did not change with the concentration; so it is a monomolecular one. At 65°, for instance, $k = 0.0097$ for a solution of 2.5 grms. of the oxime in 50 as well as in 100 c.c. of 93.6 per cent sulphuric acid (time in minutes; transformation of half of the oxime after one hundred and sixty minutes).

The transformation velocity increases with the concentration of the acid as shown from the following table:—

Temperature 60°.	Velocity-constant.	Time of half transformation.
Concentration H_2SO_4 .		
93.6	0.0011	275 mins.
94.6	0.0013	232 "
97.2	0.0038	75 "
98.7	0.0070	43 "

At 65°, 86.5 per cent sulphuric acid gave a constant of 0.0006 (time of half transformation = 501 minutes). When using 99.2 per cent acid at 60°, practically all the oxime had been converted after fifteen minutes.

The influence of the temperature is apparent from the following figures:—

At 60°, 93.6 per cent H_2SO_4 , $k = 0.0011$; 94.6 per cent H_2SO_4 , $k = 0.0013$.

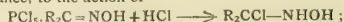
At 65°, 93.6 per cent H_2SO_4 , $k = 0.0097$; 94.6 per cent H_2SO_4 , $k = 0.0021$.

The temperature coefficient for 10°, is therefore about 3. A solution of SO_2 in chloroform did not appear to cause any transformation of the oxime.

The results of this research therefore confirm the view that in the Beckmann transformation we are dealing with a real intramolecular rearrangement. Even if the application of sulphuric acid should cause the formation of an intermediate compound (which has not yet been positively proved, but which is very probable*) our experiments show that this formation (or the conversion I. into II.) takes place with immeasurably great velocity. The very perceptible development of heat which occurs on mixing the oxime with the concentrated sulphuric acids also points to this fact.

Addendum.—Of late years, Stieglitz and his co-workers (*Am. Chem. Journ.*, 1896-1903) have been engaged in the study of the Beckmann rearrangement. In my opinion Stieglitz's ideas cannot be accepted in their entirety. Recently this chemist has given a summary of his conclusions in a separate article on the "Beckmann Rearrangement" (*Am. Chem. Journ.*, 1903, xxix., 49). He then arrives at the following views:—

The analogy of the Hofmann transformation of the amides into amines with the Beckmann rearrangement—an analogy first pointed out by Hoogewerff and Van Dorp (*Rec.*, vi., 373; viii., 173)—and the fact that the acid azides of Curtius are converted with elimination of nitrogen into the same isocyanates which occur as intermediate products in the Hofmann transformation, induces Stieglitz to attempt to explain these reactions from a same point of view. He believes that in the three above transformations there must be formed intermediate molecule residues containing univalent nitrogen; with the azides, for instance, $\text{CH}_3\text{CO.N.N}_2 \rightarrow \text{CH}_3\text{CO.N} + \text{N}_2$; with the bromamides, for instance, $\text{CH}_3\text{CONHBr} \rightarrow \text{CH}_3\text{CO.N} + \text{HBr}$. These molecule residues are then supposed to be converted straight into the isocyanate, $\text{CH}_3\text{CO.N} \rightarrow \text{CONCH}_3$. In order to arrive, in the transformation of oximes into amides, at such molecules with univalent N atoms, Stieglitz assumes that first of all HCl is attached to the oxime, owing, for instance, to the action of—



this additive compound, under the influence of PCl_5 , then loses one molecule of water, and gives $\text{R}_2\text{CCl}-\text{N}$, which molecule residue is then supposed to be converted into $\text{RCCl}=\text{NR}$, which on treatment with water yields the amide.

Now, first of all it is difficult to see where the HCl, which gets attached to the oxime, is to come from; it is of course known that some oximes yield with PCl_5 compounds such as R_2CClN with formation of HCl, but this is not the formation which Stieglitz had in mind. We also fail to see how sulphuric acid, acting as dehydrating reagent, will, in the rearrangement, cause a molecule of water to be first attached, and then to be again eliminated; neither do we understand how the transformation under the influence of, say, P_2O_5 or ZnCl_2 , can be reconciled with the ideas of Stieglitz. Finally, Stieglitz himself admits of his own theory that "it does not agree so well with the more obscure relations of the theory of stereoisomerism of ketoximes and their influence on the rearrangement of these isomers. It is hoped that future work will remove this difficulty" (*Am. Chem. Journ.*, [7], xxix., 67). The difficulty is this, that Stieglitz's theory utterly ignores a fact of fundamental importance, namely, the formation of two different amides from the stereoisomeric ketoximes; these according to Stieglitz ought to lead to the same intermediate product from which the same amide only could be formed.

* If to an ethereal solution of the oxime is added a solution of sulphuric acid in ether, a precipitate is obtained, the nature of which will be investigated.

And finally the transformations of an oxime into the isomeric amide without any reagent whatever, as observed by Werner and his co-workers, by Posner, and by Auwers and Czerny, are directly opposed to his representations.

In his last theoretical paper, Stieglitz attributes the transformation of some more hydroxylamino derivatives to the intermediary formation of molecule residues with univalent nitrogen; he includes all these under the name of "Beckmann arrangement."

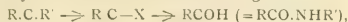
I think I have shown that this classification is not permissible. If it were so the Hofmann transformation might claim priority over the "Beckmann arrangement," which is of more recent date.

In order to avoid confusion I think it absolutely necessary to let each of the said transformations retain its own name and to treat them as separate reactions. In the Curtius transformation, $\text{CH}_3\text{CON}.\text{N}_2 \longrightarrow \text{CONCH}_3 + \text{N}_2$, the assumption of the intermediary occurrence of a molecule residue $\text{CH}_3\text{CO.N}$ is permissible; in the Hofmann reaction, $\text{CH}_3\text{CONHBr} \longrightarrow \text{CONCH}_3 + \text{HBr}$ such is



possible but not necessary; NCH_3 may also have

been formed as an intermediate product (Hantzsch); finally we may admit in the Beckmann rearrangement—



($\text{X} = \text{Cl}, \text{Br}, \text{OH}, \text{or } \text{SO}_3\text{H}$ [respectively H_2SO_4], OCOCH_3), a same mechanism as in the Hofmann transformation, but, according to my opinion, not the presence of a molecule residue with univalent nitrogen.

The physico-chemical investigation of the Beckmann rearrangement is being continued.

NOTICES OF BOOKS

Directions for Laboratory Work in Physiological Chemistry. Second Edition. By HOLMES C. JACKSON, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1903.

The second edition of this manual of practical physiology has been thoroughly revised, and some additions, which experience showed to be desirable, have been made to it. The fact that it is designed mainly for the use of medical students explains, and also justifies, the special emphasis which has been laid on some parts of the subject, which is treated most thoroughly and systematically. The concise and explicit descriptions of the experiments are such as to make the book eminently fitted for being placed in the hands of students, though the practice of constantly introducing hints by means of questions interspersed in the text, which is regarded with such great favour by some teachers, is perhaps rather overdone here. Some account of the detection of the various elements in the compounds most frequently met with in organic nature would have made the book more complete, but on the whole the subject is presented in a thoroughly scientific aspect, and the book is well suited to its purpose.

A Laboratory Manual of Physiological and Pathological Chemistry. By Dr. E. SALKOWSKI. Authorised Translation from the Second German Edition by W. R. ORNDORFF, A.B., Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1904.

The original edition of this book was rightly received most favourably in Germany, and a translation of it into English will no doubt be equally welcome in our own land. Though the text might be regarded as open to criticism in some comparatively unimportant details, among which might be

mentioned, for example, the inclusion of pages devoted to the preparation and standardisation of normal solutions, which ought to have been made familiar to the student of physiology by means of a preliminary study of pure chemistry, yet on the whole the book will be found to be unrivalled, especially for guidance in advanced work. For many reasons it is less suited to elementary students, chief among them being a certain want of system displayed in places, and the brevity of some of the directions for the experiments, but in other respects and for other purposes it can hardly be too highly recommended, and will no doubt be regarded as practically indispensable by physiologists and advanced medical students.

Elementare Vorlesungen über Telegraphie und Telephonie. 6. Lieferung. ("Elementary Lectures on Telegraphy and Telephony." Part VI.). By Dr. RICHARD HEILBRUN. Berlin: Georg Siemens. 1903.

THE sixth number of these lectures concludes the description of the Morse system, and deals fully with the Hughes apparatus, which is described as simply and intelligently as possible. It may safely be said that these lectures could not be improved upon, and post office and telegraph officials could not do better than study them with the utmost thoroughness. They will be found to contain all that is necessary for a satisfactory acquaintance both theoretical and practical (as far as it can be acquired from books) with the subject, and the author cannot be too highly congratulated on the interesting manner in which he has treated telegraphy and the eminently readable little book he has produced, which, though it might truly be styled popular in one sense, is thoroughly scientific in all its explanations, and contains no slipshod or only approximately accurate statements, as is so often the case with elementary treatises of this kind.

Die Elektrometallurgie der Alkalimetalle. ("The Electro-metallurgy of the Alkali Metals"). By H. BECKER. Halle-a-S.: Wilhelm Knapp. 1903.

THIS monograph on the preparation of the alkali metals gives for its size a very complete account of the subject. A short introduction describes early attempts at the extraction of the metals potassium and sodium by chemical means, but the greater part of the book is devoted to electro-chemical methods, which are grouped into two divisions—electrolytic and electrothermic. Sodium is naturally treated at the greatest length, and the references to current and patent literature throughout are very complete, useful notes being given on articles of special importance, such as, for instance, the paper by M. Le Blanc and J. Brode on the electrolysis of caustic soda, which appeared some time ago in the *Zeitschrift für Elektrochemie*. Potassium and lithium and electrothermic methods, having regard to their comparative unimportance, receive but little attention, and an appendix contains some hints on the apparatus most conveniently employed in the laboratory for the purpose of preparing the alkali metals.

Quantitative Analysis for Mining Engineers. By EDMUND H. MILLER, Ph.D. New York: D. Van Nostrand Company. 1904. Pp. 137.

The volume before us is one for specialists only, as it deals with quantitative chemical analysis only as applied to a limited section of the Mining Engineer's work. It consists entirely of a series of articles which appeared in the *School of Mines Quarterly*, vol. xxx.

The author explains that no attempt is made to cover the entire field of inorganic analysis, but a few important analyses are given in considerable detail. A little knowledge is a dangerous thing, and a student who had gone even carefully through this book would be in the unfortunate position we have hinted at, and at the same time

might consider himself competent to take up the position of chemist at some mining or metallurgical works.

As a book of reference in particular cases this volume may be useful, though such important subjects as gold and silver assaying are omitted.

There is no index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 22, May 30, 1904.

Chemical Effects of Light. Action of Hydrochloric Acid on Platinum and Gold.—M. Berthelot.—The author makes a series of experiments on the chemical effect of light, and finds that pure platinum is slowly attacked by fuming hydrochloric acid under its influence. The presence of manganous chloride assists the reaction considerably. In fact, the reaction is double in proportion if the chloride is present. Its presence is, however, not indispensable. Light apparently acts in these cases in the same manner as atmospheric air when the latter is used as an oxidiser for organic compounds. It seems to cause the fixation of free oxygen, which replaces the chlorine of the hydrochloric acid. Viewed in this manner, the action can also be compared to that of electrolytic oxygen.

Solubility of Silicon in Silver. A variety of Crystalline Silicon which is Soluble in Hydrofluoric Acid.—H. Moissan and F. Siemens.—The authors find that silicon is much more soluble in silver than in either lead or zinc. On crystallising out the silicon from its solution in silver the solidified metal is found to contain a certain proportion of an allotropic variety of silicon which is soluble in hydrofluoric acid.

Formation of Vanadium Ores in Nature.—A. Ditte.—Lead vanadate is almost the only vanadium ore found in nature in abundance. This mineral is found either simple or combined, as in lead chlorovanadate. The author accounts for this fact by considering the action of natural waters which circulate both hot and cold, under a more or less pressure, under the earth's crust. The disintegrated rocks, containing considerable quantities of vanadium, cause this water to become charged with vanadic acid and vanadates more or less soluble in water. These vanadium-charged waters come in contact with the principal minerals—galena, anglesite, cerusite, &c.,—which are partially transformed into lead vanadate, in which the vanadium from the different minerals in which the metal was originally distributed amongst the rocks is concentrated.

Synthesis of a Series of Tertiary Alcohols Derived from Cyclohexanol.—Paul Sabatier and Alph. Mailhe.—The authors synthesise the tertiary alcohols derived from cyclohexanol by the action of cyclohexanone on organo-magnesium compounds derived from the reaction of magnesium on fatty or aromatic halogen derivatives. Cyclohexanone reacts briskly, and if the solid crystalline mass obtained is decomposed by iced water the alcohol is prepared, usually with a good yield, $\text{CH}_2<\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{CH}_2-\text{CH}_2 \end{smallmatrix}>\text{COH-R}$; R being the aromatic or fatty residue which constituted the organo-magnesium compound.

Acetylenic Aldehydes. New Method of Preparation. Action of Hydroxylamine.—Ch. Moureu and R. Delange.—The authors prepare the acetylenic aldehydes, $\text{R}-\text{C}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)_2$, by the action of ethylmagnesium bromide or methylmagnesium iodide in etheral solution on an acetylenic hydrocarbon in a reflex condenser. After twenty-four hours of boiling, the gaseous evolution having

completely stopped, a small excess of orthoformic ether is added and the whole again heated for twenty-four hours. Finally, the mixture is cooled with iced water, and the acetal remains in the ether layer and can be extracted by distillation. The yields of the acetals are about 75 per cent.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxix., Nos. 20—21.

Chemical Equilibrium between the Ferro- and Ferri-hydrocyanic Acids.—Maurice Prud'homme.—Already inserted in full.

Chemical Equilibrium between the Ferro- and Ferri-cyanides of Potassium in the presence of Alkalis.—Maurice Prud'homme.—Already inserted in full.

The Preparation of Glutaconate of Ethyl.—E. E. Blaise.—The usual method adopted for the preparation of glutaconate of ethyl is the etherification of glutaconic acid obtained according to MM. Conrad and Guthzeit's method. This method, however, is troublesome and expensive, and the author has found, in the dehydration of β -oxyglutarate of ethyl a process which is much more practical and economical; the oxyglutaric acid being prepared by the hydrogenation of acetonedicarbonic acid.

Methylation of Glutaconate of Ethyl.—E. E. Blaise.—Already noticed.

Condensation of Glutaconate of Ethyl.—E. E. Blaise.—Already noticed.

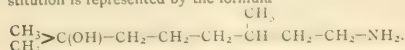
Synthesis of 2-2-dimethylglutaric Acid.—E. E. Blaise.—Already noticed.

Preparation of Adipic Acid.—L. Bouveault.—Finding the older methods inadequate the author has had recourse to the electrolysis of a very concentrated aqueous solution of ethylsuccinate of sodium, and here again he found the results low compared with the energy exerted, owing to the increase of resistance caused by the heating of the solution. Eventually, after making considerable modifications in the apparatus and method employed, he succeeded in getting a better return of adipate of ethyl, though it did not exceed 40 per cent. Finally by the electrolysis of succinic anhydride he succeeded in obtaining a regular return of 70 per cent of pure adipate of methyl. To transform this adipate of methyl into adipic acid it is heated for ten hours in a steel autoclave at 200° with ten times its weight of water. Alkaline saponification must be avoided because of the difficulty of separating the adipic acid from the salts with which it is mixed, which difficulty is caused by its greater solubility in water than in ether or any other solvent not miscible with water.

The Secondary Products of the Electrolytic Preparation of Adipic Acid.—L. Bouveault.—Among the secondary products of this reaction described by the author is β -oxypropionate of ethyl, which is split up into iodide of ethyl and β -iodopropionic acid when treated with gaseous hydroiodic acid. Another body is adipate of ethyl, and another is a tribasic acid with the formula $\text{C}_{15}\text{H}_{26}\text{O}_6$. A further body obtained is an acid succinate of ethyl having the formula $\text{C}_9\text{H}_{16}\text{O}_4$, while an oily liquid, boiling at 194° at 20 m.m., has the formula $\text{C}_{12}\text{H}_{20}\text{O}_6$.

On Rhodinamine.—L. Bouveault.—The author describes the preparation of a new body he calls rhodinamine, which differs from rhodinol only by the changing of the oxyhydrile into an amidogen group. This rhodinamine is capable of combining with one molecule of water under unexpected conditions which were first discovered by accident. The first time it was prepared he was attempting to dry the etheral solution by means of powdered solid potash. The ether, when distilled off, left a slightly viscous liquid which did not contain a drop of rhodinamine, and boiled at 140° at 15 m.m. Analysis showed that the base had combined with 1 molecule of

water, forming a tertiary amine-alcohol of which the constitution is represented by the formula—



Hexahydrobenzoic Aldehyde, Hexahydroacetophenone and the Corresponding Secondary Alcohol.

—L. Bouveault.—The author has recently prepared the hexahydrobenzylic alcohol by treating hexahydrobenzoate of ethyl with sodium and absolute alcohol. He oxidised this alcohol to obtain the corresponding aldehyde, but the return is low, as part of the alcohol is oxidised to the state of hexahydrobenzoic acid, and part to the state of hexahydrobenzoate of hexahydrobenzyl. The hexahydroacetophenone, $\text{C}_6\text{H}_{11}\text{---CO---CH}_3$, is a colourless liquid boiling at 68° under 12 m.m. It has a fresh, agreeable odour, recalling that of the fatty acetones of similar molecular weight. It combines readily with bisulphide of sodium, giving a crystallised compound, decomposed by the alkaline carbonates. It is very difficult to obtain free from water.

Action of Oxygen on the Organo-halogen-magnesian Derivatives.—L. Bouveault.—A molecule of chloride of benzyl, dissolved in ether, was treated with an atom of magnesium in a flask fitted with a bromine tube and a vertical condenser. When the reaction was over the bromine tube was replaced by a tube terminating in a funnel and plunging into the liquid, and perfectly dry pure oxygen was passed through. The oxygen was absorbed integrally with the evolution of sufficient heat to keep the ether boiling for the two hours the reaction lasted. On cooling, the liquid thickened rapidly and became changed into a solid white mass, consisting, no doubt, of the compound $\text{C}_6\text{H}_5\text{---CH}_2\text{---O---Mg---Cl}$. This mass was treated with water, then with dilute sulphuric acid; the ethereal solution which separated out was washed and distilled, and an 80 per cent return of perfectly pure benzylic alcohol was obtained.

Chlorination of *p*-Amido and *p*-Oxy-*o'*-*p'*-dinitrophenylamine by means of Chlorate of Sodium and Hydrochloric Acid.—F. Reverdin and P. Crépieux.—A long paper in which the authors describe their methods, and give analyses of the products obtained.

Purification of Natural Mineral Waters by means of Carbonate of Barium.—G. Arth and P. Ferry.—The authors find that both the lime and magnesia are precipitated by boiling with carbonate of barium, though the magnesia does not disappear to any great extent; for example, with two molecules of the carbonate and seventy-two hours' agitation at the ordinary temperature there was a loss of 50 per cent of magnesia, and after six hours' boiling the loss was only 36·6 per cent.

MISCELLANEOUS.

Examination of Nitrifying Microbes.—E. Boulanger and L. Messol.—The authors have examined the conditions of culture of the nitric and nitrous ferments. The nitrous ferment is killed by heating to 45° for five minutes; the nitric ferment to 55° ; the best temperature for the cultivation of both ferments is 37° . The nitrification is accelerated by cultivating the ferments on coke placed in revolving barrels. The production of nitrite is arrested in liquids containing 30 to 50 grms. per litre of sulphate of ammonia, it is retarded by 8 or 10 grms. of nitrite of magnesia, and stopped by 13 to 15 grms. The nitrates of soda and potash interfere in doses of 1 to 5 grms. per litre. Those of lime and magnesia at 1 per cent at least. The transformation of nitrites into nitrates is made difficult by the concentration of the medium in nitrite or nitrate; it is stopped by a dose of 20 grms. per litre of nitrite or 25 grms. of nitrate. Nitrate of lime retards nitration in a

dose of 12 grms. per litre.—*Ann. de l'Institut Pasteur*, vol. xvii., No. 7, p. 492.

The Maximum Density of Aqueous Solutions of some Organic Bodies.—W. Mueller.—The addition of water to organic bodies of different compositions (phenol, pyrocatechin, resorcin, hydroquinone, pyrogallol, phloroglucin, mannite, glucose, oxalic, succinic, and tartaric acids) gives rise, at the temperature of maximum density, to very different molecular lowerings. As in the mineral bodies already studied from this point of view, the lowering observed is nearly proportional to the concentration of the solution (alcohol is an exception to this law); however, we observe in the case of most of the bodies examined, that the molecular lowering increases a little with the concentration, and this variation is not sufficiently slight to be explained by errors of experiment. It is apparently caused by a partial association of the molecules of the substance dissolved. The variation of the maximum of density does not appear to depend only on the molecular weight of the substance dissolved; its chemical constitution also exercises a considerable influence. This variation increases with the number of hydroxylised groups; it augments (at equimolecular concentrations) in the series, phenols, diphenols, triphenols; also in the series, succinic acid, tartaric acid. The three diphenols give nearly the same value; there is a little greater difference between the two triphenols. Finally, the increase of the molecular lowering with the concentration, very marked in the case of the ortho-phenol, is slight with the meta-, and does not occur at all with the para-phenol. This result is explained by the tendency of pyrocatechin to give double molecules in concentrated solutions, a tendency which is only found in a less degree with resorcin, while it no longer apparently exists in the case of hydroquinone.—*Zeit. Physik. Ch.*, vol. xliii., p. 109.

The State in which some Superoxygenated Acids and their Salts exist in Solution.—L. Pissarjewsky.—The superoxygenated acids obtained by the action of peroxide of hydrogen (pertungstic, permolybdic, peruranic acids) give off peroxide of hydrogen when they are destroyed by an acid. For this reason the author is inclined to look upon them as salts of this peroxide. To justify this hypothesis, he determined the manner in which the salts of these acids are decomposed in aqueous solution, by the method of parting with ether, and by measuring the conductivity. Thus, he found that the peruranate UO_8Na_4 is a salt of the feeble acid $\text{UO}(\text{OH})(\text{O}_2\text{H})_2$; in aqueous solution it is hydrolysed into NaOH and H_2O_2 , and phenomena of equilibrium take place between the undecomposed salt and its products of decomposition. On standing this solution gives a deposit of the acid $\text{UO}(\text{OH})(\text{O}_2\text{H})_2$, which is but slightly soluble. Solutions of pertungstic acid contain the acids $\text{WO}_2(\text{OH})(\text{O}_2\text{H})$, $\text{WO}_2(\text{O}_2\text{H})_2$, and probably also at a low temperature, $\text{WO}(\text{OH})(\text{O}_2\text{H})_3$ and $\text{WO}(\text{O}_2\text{H})_4$. The two first of these acids are hydrolysed in aqueous solution, with the formation of peroxide of hydrogen. As for the pervanadates $\text{V}_5\text{O}_{26}\text{K}_8$, the first is a salt of a monobasic acid, and the second a compound of the salt of pyropervanadic acid, which is quadribasic, and of that of metapervanadic acid, which is monobasic. The aqueous solutions of perborate of sodium at 25° contain BO_2Na , NaOH , Na_2O_2 , BO_3H_3 , H_2O_2 , and traces of BO_3Na . This latter salt forms in quantities which are greater as the temperature is lower; at 0° the solution contains nothing but this salt.—*Zeit. Physik. Ch.*, vol. xliiii., p. 160.

Use of N-rays in Chemistry.—H. Becquerel.—The author finds, as was predicted from an examination of the Blondlot radiations, that there are two orders of chemical phenomena according as, say, alkalis act on metallic sulphates or metallic sulphates act on alkalis, and these two orders of chemical phenomena correspond to the two methods of emission. The experiments were made with baryta in aqueous solution and at ordinary temperatures.—*Comptes Rendus*, cxxxviii., No. 23.

BATTERSEA POLYTECHNIC, S.W.

The Governing Body require the Services of a LABORATORY STEWARD and LECTURE ASSISTANT in the University Department (Day and Evening).—For particulars send stamped addressed envelope at once to the SECRETARY.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

ASSISTANT LECTURER AND DEMONSTRATOR IN CHEMISTRY.

The Council invite applications for the Post of ASSISTANT LECTURER and SENIOR DEMONSTRATOR in CHEMISTRY.

Applications, together with copies of testimonials, should reach the undersigned, from whom further particulars may be obtained, not later than SATURDAY, JULY 9, 1904.

T. MORTIMER GREEN, Registrar.

June, 1904.

To CHEMISTS (METALLURGICAL & ANALYTICAL).

A well-arranged Suite of Laboratories, with an Office attached, To Let in Victoria Street. The laboratories newly fitted with all the latest improvements and conveniences for Analytical work. Gas and Electric current, and good Water supply. £120.—Apply, Secretary, 34, Victoria Street, London, S.W.

Chemical Works, manufacturing Chemical Manures on a large scale. Recent death of a Director leaves vacancy on Board for a Gentleman having £5000 to £7000 to invest. Security certain.—Write "Chemical," care of Gould's Advertising Agency, 54, New Oxford Street, London.

Wanted in a Chemical Laboratory in London, a Student-Assistant (sixth on staff). Applicants, who should preferably not be more than twenty-one years of age, should have studied at one of the colleges recognised by the Institute of Chemistry, and should have satisfied the requirements of the Institute in regard to preliminary training. The work is of a varied nature, and the selected candidate would obtain a good training in one or two branches of Applied Chemistry, and there would be a prospect of promotion. A small salary would be given to a suitable man.—Address, "Analyst," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

To WHOLESALE MANUFACTURING CHEMISTS.

Wanted, complete information as to Camphor Refining. Sodium Hydrate Stick Moulding, or other Chemicals of profitable nature, by firm in N.E. Lancashire.—Address, in confidence, J. J. CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC. As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, &c.

E. GEORGE & SONS,
BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.

Are OPEN to PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1890, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION. FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.
LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.

RADIUM

ON SALE AND LET ON HIRE.—Write for terms.

The following can be had by return of post.

Pitchblende, direct from Joachimsthal, very radio-active, from 1/- to 30/- per piece.

Itacolumite, or flexible sandstone, 10/- to 25/- per piece (very rare).

Kunzite, 1/- per gramme. Selected, clear, 2/-

Spartite (see NATURE, 31/3/04, fol. 523), 2/- and upwards.

Chlorophane, 2/- and upwards. Barium Platino Cyanide in large Crystals in course of manufacture. (ORDERS BOOKED).

Zinc Sulphide. Phosphorescing a beautiful Green, 2/6 per tube.

" " " " Yellow, 2/6 " " " " Violet, 1/- " "

Radio-active Residue from which Radium is made; very scarce, 2/- tube.

Potassium Sulphide, in tubes of one gramme, 21/-

" on Bismuth Rod or Disc, " " " 25/-

" on Copper " " " 25/-

Radio-active Screens (Willmetite), 6d. per sq. inch. Plat. Bar. Cyan Screen, 9d. sq. inch. (Zinc Sulph.), 10 x 10 cm. 7/6.

Professional Men, Universities, Schools, &c., allowed special terms

Our newly invented Thorium Inhalers may be had on hire.

ARMBRECHT, NELSON & CO.,
71 & 73 DUKE ST., GROSVENOR SQ., LONDON, W.

Telephone: GERRARD 4942.

N.B.—We have to-day received a consignment of the New Zealand Vegetable Caterpillar; it is from 2 to 3 inches long, with a stem showing fructification growing out of its head. Scientific name of the insect is *Hepialus virescens*; the name of the fungus is *Sphaeria Robertiana*. Specimens may be had from 10/6 to 21/-, according to quality and size.

TERMS CASH WITH ORDER.

Goods may be returned if not approved of, when money will be refunded.

BRYAN CORCORAN LIM.

MILLSTONE BUILDERS.

WIRE WEAVERS, MACHINE MANUFACTURERS AND GENERAL MILL FURNISHERS.

Sole Makers of MILBURN'S

Patent Conoidal Stone Grinding Mills.

Especially suitable for certain materials, Wet or Dry.

Works and Showrooms: Back Church Lane.

Parcel Dept.: Basement of the Corn Exchange.
31, MARK LANE, LONDON.

**OLD PLATINUM**

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver Refiners, &c., 40 and 42, Clerkenwell Ed., E.C.

Photographic Residues reduced and Purchased.

**COVERS FOR BINDING.**

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGDON ST., E.C.

THE CHEMICAL NEWS.

VOL. XC., No. 2328.

ON FLAME SPECTRA.*

By CHARLES DE WATTEVILLE.

In order to obtain the spectrum of any substance, it has generally been considered sufficient to introduce a small quantity of it into an already formed flame. In the course of a photometrical investigation of flames which had been coloured by injecting the spray from saline solutions into the gas to be burnt, M. Gouy discovered in the spectra of the flames several new lines belonging to the metal contained in the solution (*Annales de Chimie et de Physique*, 1879, 5th Series, vol. xviii.). Instead of appearing throughout the whole flame, as did the previously known lines, these new lines were only emitted in the vicinity of the inner blue cone—the origin of the Swan spectrum. The observations of M. Gouy were limited to the examination of certain lines of the visible portion of the spectrum, and, with the advice of Professor Schuster, and under his direction, I have taken up this study with the object of extending it, by means of photography, to the ultra-violet portion of the flame, and also of detecting lines which are too feeble to be visible to the eye.

The method employed for the production of the flame is, in short, that which has been introduced by M. Gouy and described by him in his memoir, to which reference should be made for a description. The very slight modifications which have been made in the apparatus of this scientist are due to the necessity of having an arrangement which should be as automatic as possible during the eight hours which were often found necessary for the photographic exposures. These modifications, however, have an important bearing upon the success of the experiments.

The spectroscopical apparatus used has been of two kinds—a fine Rowland concave grating of 1-metre radius and prism spectroscopes. The results obtained by means of the grating have been completed, as regards the very weak lines, with the help of the prism spectroscope.

The lines in the spectra obtained under the conditions of my experiments are very much more numerous than is the case when all the portions of the flame do not participate in the production of the phenomena. Not only are all the lines present which were seen by Professor Hartley in the oxy-hydrogen blowpipe flame, but, in addition, there are a large number of other lines which only extend to the height of the blue inner cone. Moreover, the flame spectra extend sufficiently far into the ultra-violet in order to enable the line 2194 of tin to be observed.

If we compare the flame spectra thus produced with those of the arc and the spark it will be noticed that, as a rule, the lines which are found in the flame spectrum are those which are the strongest lines in the arc spectrum. In certain cases some of the more intense arc lines are absent, whereas less intense arc lines are to be found in the flame spectrum. On the other hand, none of the characteristic lines of the spark spectrum are ever seen in the flame spectrum. The resemblance, however, is very marked between the flame spectrum and that of the spark which has been made oscillatory by the introduction of a self-induction into the discharging circuit of a condenser. In the latter case, as is well known from the work of Dr. Hemsalech, the spark spectrum is considerably simplified ("Sur les Spectres d'Étincelles," Paris, Hermann). Moreover, although the flame spectrum will contain only the lines which belong to the spectrum of the oscillatory spark, yet all the lines of the latter will not be found in the flame spectrum, the missing lines being those which are

peculiar to the ordinary spark spectrum, and which only exist in the immediate neighbourhood of the electrodes, becoming shorter and shorter, and finally disappearing as the self-induction is increased.

The preceding paragraph refers to metals other than those belonging to the iron group. On the contrary, there is a most striking similarity between the flame spectra of iron, of nickel, and of cobalt, and the oscillatory spark spectra of the same metals in the region included between about 4300 and 2700 Angstrom units. The similarity of the two spectra is so great that, except for very small differences of intensity, the oscillatory spark spectrum, which is photographed as a comparison spectrum in the centre of the flame spectrum, appears to be a prolongation of the latter. It should be noticed that if in the visible portion of the spectrum certain lines appear to be missing, it is doubtless because the continuous spectrum prevents these feeble lines from being seen. This explains why M. Gouy was not able to observe the nickel lines which are found on the photographs taken with various salts of nickel, viz., the sulphate, chloride, and ammoniacal chloride. In the ultra-violet the spectrum of the flame appears to fade away a little more rapidly than that of the oscillatory spark, but it is probable that this difference would be reduced by prolonging the time of exposure, since it is, of course, the radiations of the shortest wave-length which are most absorbed by different media.

It is very probable that the reason for this similarity between the spectrum of the flame and the spectrum of the oscillatory spark is entirely a question of temperature. On the one hand, the increase in the number of lines of the flame spectrum obtained by the use of the sprayer may be attributed to the fact that the hottest regions of the flame take part in the production of the phenomena, and, on the other hand, the diminution in the number of lines in the spark spectrum when the spark becomes oscillatory is due to a diminution of its temperature.

THE DECOMPOSITION OF AMMONIA BY HEAT.*

By E. P. PERMAN, D.Sc., and G. A. S. ATKINSON, B.Sc.

THIS subject has been already dealt with by Ramsay and Young (*Journ. Chem. Soc.*, 1884, vol. xlv., p. 88) who heated ammonia in glass tubes at various temperatures, and found that decomposition began under the most favourable circumstances at a little below 500°, and that the amount decomposed depends on the extent of the heated surface of the solid with which the ammonia is in contact, on the nature of the surface, and on the time of exposure to heat.

We have thought it desirable to extend our knowledge of the subject still further by investigating the rate of decomposition at various temperatures. The ammonia was contained in porcelain vessels heated in a muffle furnace, and the decomposition was traced by reading the pressure on a mercury manometer, the sum of the volumes of the ammonia, and products of decomposition being kept constant. The difficulty of finding the amount of ammonia in the vessel at the beginning of the decomposition was overcome by heating the ammonia at the end of a series of observations until complete decomposition was caused; the pressure and temperature were then noted, and the original amount of ammonia calculated. We have confirmed the observations of Ramsay and Young that the decomposition is never absolutely complete, but after heating at a temperature of 1100° for a short time the amount of ammonia remaining is so small that it can be neglected for practical purposes.

Apparatus.—The ammonia was heated in a porcelain globe A (Fig. 1) of about 2 litres capacity by means of a muffle furnace, B; the capillary stem of the globe was connected with a capillary glass tube by a copper sleeve and

* Abstract of a Paper read before the Royal Society, June 16, 1904.

* A Paper read before the Royal Society, June 16, 1904.

some fusible alloy. The pressure gauge D stood 2 metres high, and the level of the mercury was regulated by a movable reservoir, F. The pressure was read on a millimetre scale; G is a movable piece of mirror glass of rectangular shape, and with a horizontal line drawn across it; by sliding it along the edge of the millimetre scale and behind the glass tubes of the gauge, the readings were made with great facility.

H is a U-tube with a stopcock at the bottom; its object was to cut off the ammonia from the three-way stopcock K by a column of mercury, and so prevent or indicate leakage. One branch of the stopcock K led to a water-air pump, and the other to a long tube L containing caustic soda, and thence to a cylinder of ammonia with a safety escape M, consisting of a tube dipping into a column of mercury.

was found to be free from carbon dioxide. A quantity of pure hydrochloric acid was neutralised by passing the gas from the cylinder through it, and the solution was then evaporated to dryness. Chlorine was then estimated in the sample by the gravimetric method, and the percentage found was (1) 66.09; (2) 66.12; mean, 66.105; theoretical, 66.23.

Method of Work.—The furnace was heated, and when the temperature was sufficiently constant, the filling process was commenced. The globe was exhausted, and ammonia admitted from the cylinder through the drying tube L; this was repeated from eight to ten times, when the filling was regarded as complete. Readings of pressure were then made at definite time intervals, and the temperature was also carefully noted, as nearly as possible at the same time, by means of the pyrometer. In one or two of the experi-

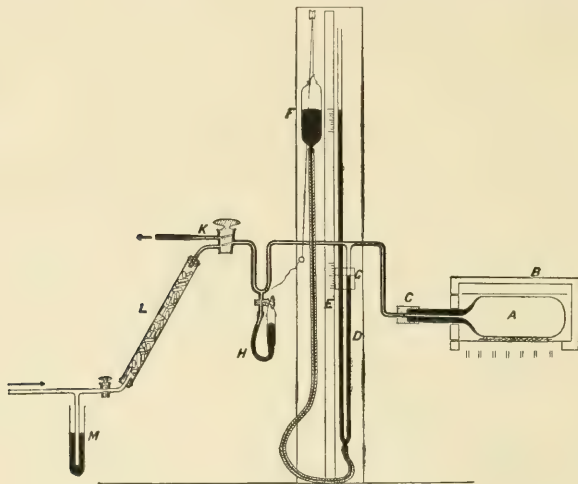


FIG. 1.

Measurement of Temperature.—Temperature was measured by means of a Callendar-Griffiths pyrometer. The disturbing effect of the current of hot air passing over the projecting head of the thermometer was avoided by surrounding the head with several turns of tinned iron. The temperatures were read to 0.1° C. The thermometer was carefully standardised with melting ice, boiling water, and boiling sulphur, and we do not think that the temperature error can in any case exceed 0.5° C.

Thermostat.—To maintain the temperature constant an Ostwald pattern regulator was used, the vessel being of porcelain, and containing air. In addition to this a Fletcher gas regulator was fixed on the main supply. Any variation of temperature caused by alteration of the barometric pressure was corrected by means of a screw at the bottom of the U-tube containing the mercury. It was found convenient to adjust the gas supply to give the required temperature by loading the valve of the Fletcher regulator.

Material.—The cylinder of ammonia was obtained from the Standard Anhydrous Ammonia Company, and was found to contain but very little impurity. In one experiment about 20 litres of ammonia were passed slowly through a long worm surrounded by ice and hydrochloric acid, but nothing appreciable was condensed. The gas

remains the temperature was sufficiently high to decompose the ammonia completely in a short time, but in most of them, when a sufficient number of readings had been made, the temperature was raised until (practically) complete decomposition ensued in a few minutes. The volume of the ammonia and decomposition products was kept constant by raising the mercury reservoir F so as to keep the mercury at about the same level in the upper part of the short limb of the pressure gauge. As each time interval was called, the level of the mercury in D was read, and that in the open limb as soon as possible afterwards; it did not change quickly in the latter, owing to the width of the reservoir.

Some observations were also made on the effect produced by sudden change of pressure on the rate of decomposition.

Method of Calculation.—The ultimate decomposition of ammonia is customarily represented by the equation $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$. Let p_1 be the pressure of the ammonia in the globe at any instant during the decomposition; p_1' , that of the nitrogen; p_2' , that of the hydrogen; P , the total pressure at the same instant; p_0 , the initial pressure of the ammonia at the beginning of the experiment.

Then—
$$p_1 + p_1' + p_2' = P \quad \dots \dots (1),$$

also—
$$p_2' = 3p_1' \quad \dots \dots (2),$$

and—
$$p_1' + p_2' = 2(p_0 - p_1) \quad \dots \dots (3),$$

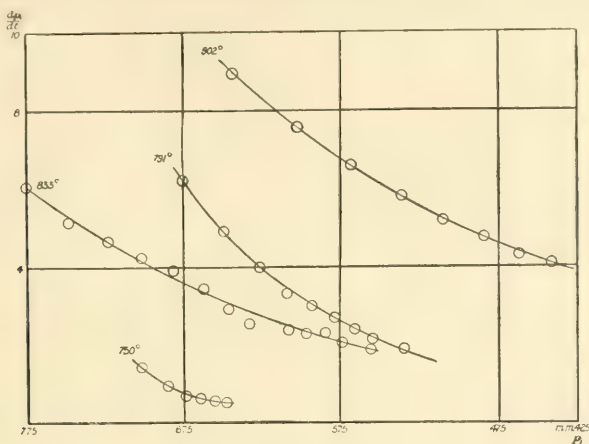


FIG. 2.

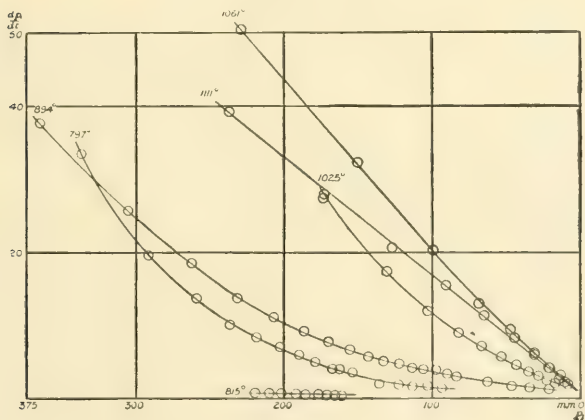


FIG. 3.

expressing that (1) the sum of the partial pressures is equal to the total pressure; (2) the pressure of the hydrogen produced is three times that of the nitrogen; (3) the sum of the pressures of the nitrogen and hydrogen is double the pressure of the ammonia decomposed.

From this it follows by substitution that $p_1 = 2p_0 - P$, i.e., the pressure of the ammonia at any instant is double the initial pressure minus the total pressure at the instant of observation. The experimental data furnish values of P and $2p_0$, and $2p_0 - P$ has been tabulated giving the pressure of ammonia at the time of observation. From these numbers corresponding values of $\Delta P/\Delta t$ have been calculated by taking the mean of the two consecutive differences and dividing by the time interval; but $P/\Delta t = dP/dt$ approximately within the limits of experi-

mental error, and $dP/dt = dp_1/dt$, and therefore we have the rate of change of the pressure of the ammonia at definite pressures, they have been plotted in two series of curves.

Results.—The rate of decomposition was found to be much influenced by the state of the globe; it invariably increased after the globe had been used once or twice, owing probably to the action of ammonia or hydrogen upon the porcelain; consequently we were not able to trace the effect of temperature on the rate of decomposition. In the first experiments the projecting stem of the globe was allowed to become too hot, with the result that a trace of the alloy at the joint c found its way into the globe, and by its catalytic action increased enormously the rate of decomposition of the ammonia. The alloy contained a small

proportion of mercury, and a film of this metal was found on the interior of the globe when it accidentally broke. In the later experiments great precautions were taken to maintain the stem of the globe at a low temperature. The experiments are here tabulated to serve as a key to the curves.

Mean temperature.	Greatest variation of temperature.	Remarks.
791°	$\pm 0.2^\circ$	Traces of mercury present.
750	0.6	
841	0.2	New "clean globe," pressure fell only 20 m.m. in 2 hours.
894	0.6	Globe as from last experiment.
833	1.1	
1111	0.35	Globe "freshly cleaned."
902	0.8	
1061	0.6	Globe as from last experiment.
815	0.4	
797	1.0	Iron wire in globe.
1025	0.4	Pt black in globe.

The measurements made at 1111° and 1025° are given in full; they may serve as samples.

Mean Temperature 1000°.			
Time.	Total pressure (P).	$2p_0 - P$.	dp_1/dt .
Mins.	M.m.		
0	1047.4	330.1	—
2	1140.7	236.8	39.2
4	1204.3	173.2	27.4
6	1250.4	127.1	20.6
8	1286.8	90.7	15.5
10	1312.3	65.2	11.4
12	1332.5	45.0	8.35
14	1345.7	31.8	6.0
16	1356.4	21.1	4.2
18	1362.6	14.9	2.7
20	1367.1	10.4	2.35
22	1372.0	5.5	—
32	1377.5	0.0	—
42	1377.5	0.0	—

It will be noted that in this experiment the decomposition was completed without raising the temperature.

Globe rinsed with a Solution of Platinum Chloride and heated to bright redness. Mean Temperature 1025°.

Time.	Total pressure (P).	$2p_0 - P$.	dp_1/dt .
Mins.	M.m.		
0	1126.1	242.4	—
2	1195.8	172.7	27.95
4	1237.9	130.6	17.4
6	1265.4	103.1	12.0
8	1285.9	82.6	9.05
10	1301.6	66.9	7.2
12	1314.8	53.7	5.8
14	1324.9	43.6	4.6
16	1333.2	35.3	3.7
18	1339.7	28.8	3.1
20	1345.5	23.0	2.5
22	1350.8	17.7	2.1
24	1354.8	13.7	2.0
26	1358.9	9.6	1.9
28	1362.5	6.0	—

$2p_0$ is taken as 1368.5, which was obtained by extrapolation of the time-pressure curve.

These results are best understood from the curves shown in Fig. 2 and Fig. 3, having values of dp_1/dt as ordinates and of p as abscissae.

Fig. 2 shows the lower and Fig. 3 the higher ratio of decomposition. The curves, as a rule, do not depart much from straight lines, and at the highest temperatures, 1061° and 1111°, become straight lines, or very nearly so. These results indicate that at the highest temperatures the decomposition is of the first order, i.e., it is monomolecular, pro-

ceeding according to the equation $\text{NH}_3 = \text{N} + 3\text{H}$; the union of the atoms to form molecules is probably so quick that it can be neglected when compared with the rate of decomposition of the ammonia molecule. The departure from this mode of decomposition at lower temperatures is possibly caused by the volume and mutual attraction of the molecules. No formula has yet been devised to express the results satisfactorily.

In the presence of substances having a catalytic action, the resulting curve is altered in character, the curvature being greater at the higher pressures. This is well shown in the curves at 750° and 791° (Fig. 2), mercury vapour being present, and in those at 797° and 1025° (Fig. 3), when iron wire and platinum black respectively were present. In these two latter experiments it will be noticed that the rates of decomposition reached and passed those without catalyser for about 100° higher.

Effect of Sudden Change of Pressure on the Rate of Decomposition.

As a final experiment the effect of a sudden change of pressure was tried, the globe containing both iron wire and finely divided platinum. The change of pressure was brought about by allowing the gases in the globe to blow off into the air for a few seconds, and a reading of the pressure gauge was made as soon as possible afterwards.

Time.	Pressure-gauge.	Bar.	Total pressure.	ΔP .
7.4	335.2	760.8	1096.0	20.8
9	356.0	"	1116.8	19.6
14	375.6	"	1136.4	
7.16	58.2	760.9	819.1	15.2
21	73.4	"	834.3	14.7
26	88.0	761.0	849.0	

The ratio of the pressures before and after the change is $1136.4/819.1 = 1.39$, and that of the ratio of decomposition (taken approximately from the values of ΔP) is $19.6/15.2 = 1.29$.

The agreement is sufficiently close to show that the reaction is essentially of the first order, or monomolecular, apart from the little understood disturbing influences (see van't Hoff's "Vorlesungen," 2nd edition, p. 234).

Summary and Conclusion.

The rate of decomposition of ammonia has been investigated under various conditions; the containing vessel was of porcelain. The temperatures varied from 677° to 1111°. It was found that the reaction is essentially monomolecular, being similar to that for arseniuretted hydrogen, as found by van't Hoff. The rate of decomposition is much quickened by the presence of traces of some of the metals, those tried being, mercury, iron, and platinum.

We are indebted to the Government Grant Fund of the Royal Society for the cost of most of the apparatus employed, and wish to express our great obligations to Principal Griffiths for the loan of some of his apparatus for platinum thermometry, and for his kind guidance in its use.

Supplementary Note, May 27, 1904.—We have assumed that the decomposition of ammonia is an irreversible reaction, i.e., $k = 0$ in the general formula $dx/dt = k(a-x)(b-x)$ $-k'(a'+x)(b'+x)$ for Ramsay and Young showed (*loc. cit.*) that on passing a mixture of dry nitrogen and hydrogen through a heated glass tube containing iron filings, or through a red-hot iron tube, no appreciable quantity of ammonia was formed, a result which we confirmed by experiments of our own some years back, obtaining the same result also with a glass tube containing porcelain. We find, however, that this view of the matter is not generally accepted; Ostwald, for instance, in his "Grundlinien der Anorganischen Chemie" (1900, p. 345) states that, on heating ammonia, equilibrium ensues when 98 per cent of the ammonia is decomposed. We should like to point out that the results of our experi-

ments, now described, show no indication whatever of any such equilibrium, for the curves all run towards the origin within the limits of experimental error, whereas, if there were any equilibrium before the ammonia was all decomposed, they would cut the horizontal axis to the left of the origin, and, moreover, the equilibrium would change with the temperature.

We have mentioned that a trace of ammonia was always found in the globe at the end of an experiment, but this probably came from the cold stem; and, moreover, since the rate of decomposition may be taken as proportional to the amount of ammonia present, that amount can, strictly speaking, never quite reach the zero point.

Whether a minute quantity of ammonia remains finally undecomposed would not be indicated by these results, and we intend to approach the subject from another direction, and to examine generally the conditions under which nitrogen and hydrogen combine to form ammonia.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 15th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. G. Dean, C. D. McCourt, J. C. Smith, R. de J. Fleming-Struthers, and C. H. Thompson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William H. R. Allen, care of Straits Trading Co., Butterworth, Penang, S.S.; Jabez Horace Cooper, 13, Victoria Terrace, Exeter; George Frederick Phillips, B.Sc., Colworth Road, Leytonstone; Edwin Roy Watson, B.A., B.Sc., 1, Fair Street, Cambridge.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Albert Ernest Bellars, B.A.; Herbert Frank Brand, M.A.; W. Edgington Field; Thomas Alfred Gerard; James Gray Gilchrist, M.A.; John Hulme; Herbert Jenkins; John Haslam Johnson, M.Sc.; Rudolf Lessing, Ph.D.; Frank Harold Lowe, B.Sc.; William Edward Oakden; Alfred Pell; David John Pinkerton; Robert Rodger; Percy Richard Sanders; Charles John Sawyer; Henry Stanley Shelton; John Weinberg; James Alfred Wilkinson, M.A.

The President stated that six of the seven Past Presidents to whom the Society desired to do special honour at the Banquet held in 1898 having passed away, the Council felt that there should be no further delay in the publication of a memorial notice of the life and work of each. Arrangements had accordingly been made for the preparation of such notices, which, it was hoped, would be incorporated in the volume of *Transactions* for the present year. The list includes the name of Frankland, concerning whom a Memorial Lecture had been delivered by Professor Armstrong at a special meeting of the Society in October, 1901. Repeated application for the manuscript having been unsuccessful, and nearly five years having elapsed since the death of Sir Edward Frankland, the Council were arranging for the preparation of an independent obituary notice.

The President further stated, for the information of the Society, that arrangements had been completed for the publication annually of Reports on the Progress of Chemistry under the several heads employed in the *Journal* for the classification of the Abstracts, with addition of a new section on "Radio-activity." It was expected that these reports, collected into an extra number of the *Journal*, would be ready for issue to the Fellows early in the spring of each year.

The attention of the Fellows was also requested to the notice inside the cover of the *Journal* relating to the Inter-

national Tables of Atomic Weights, which are now printed on cards to be obtained from the Society's Agents, Messrs. Gurney and Jackson.

Of the following papers, those marked * were read:—

*III. "The Mechanical Analysis of Soils and the Composition of the Fractions resulting therefrom." By ALFRED DANIEL HALL.

The object of the investigation was to ascertain the effect of introducing into the mechanical analysis of soils a preliminary treatment of the soil in dilute acid followed by ammonia as first suggested by Schlesinger. For the separation into fractions, the beaker method of sedimentation as worked out by Osborne was adopted, the soil being divided into two fractions by sieves and five by sedimentation from water. Eighteen soils of known history were selected from the Rothamsted experimental plots, to give comparisons of the same soil in an unmanured condition and when rich in humus through the accumulation of organic matter.

The proportions in which the groups of particles of given sizes occur in a soil are presumably constant for the particular type of soil; the actual state of aggregation of the particles at any given time or place determines what may be termed the texture of the soil and depends on a number of temporary factors, such as the cultivation to which the soil has been subjected, the amount of humus present, the use of lime or of saline manures, &c. It is held that no method of mechanical analysis can measure the existing texture of the soil, although that texture does ultimately depend on the size of the particles composing the soil. If, however, the method of mechanical analysis can be made to show the ultimate physical constitution of the soil, a measure is obtained of the capacity of the soil to acquire a known texture under given methods of cultivation.

On comparing the results obtained by sedimenting the Rothamsted soils with and without the preliminary treatment in dilute acid, it is found that the raw soil rarely yielded as much of the finest or "klay" fraction as did the same soil after washing with acid, and that the difference was greatest when pastures and other soils rich in humus were examined, but practically disappeared with soils which had been deprived of their humus and deflocculated by long treatment with saline manures. As no valid reasons exist for supposing that the acid treatment can break down large particles into smaller ones, it is concluded that in carrying out a mechanical analysis on the raw soil mang aggregates of the finest particles are left unresolved, but fall apart when the humates, which act as a weak binding material, are removed by the treatment with dilute acid followed by ammonia. A further action of the acid treatment is to remove all traces of soluble salts, which would otherwise cause flocculation and interfere with the sedimentation. It is only when dealing with soils containing a fair amount of humus that there will be much difference between the results obtained by the two methods, but, inasmuch as only the acid treatment yields an exact sorting out of the ultimate inorganic particles of the soil, whereas working on the raw soil leaves some of the finest particles still unseparated, the general conclusion is reached that the acid treatment should be adopted in all cases.

With the Rothamsted soils, the method involving a preliminary treatment with acid shows the essential identity of soils from the same experimental field whatever the manuring has been, whereas the analyses made on the raw soil give very different results, depending on the treatment the various plots have received.

Determinations made of the alumina, silica, and ferric oxide in the various fractions separated by mechanical analysis show that although the proportion of alumina increases as the particles composing the fraction become smaller, these fractions do not possess any chemical individuality, but are determined by the size and not by the chemical composition of the particles.

*112. "The Effect of the Long-continued Use of Sodium Nitrate on the Constitution of the Soil." By ALFRED DANIEL HALL.

On reviewing the results of the mechanical analysis of Rothamsted soils, it was observed that those which had been manured with sodium nitrate every year gave abnormal results; a further series of fifteen soils was examined drawn from each of the Rothamsted fields where plots with and without sodium nitrate occurred. In general, the use of sodium nitrate has resulted in a lower proportion of "clay" being left in the surface soil. This result was most manifest in the mangel field, where cultivation is frequent, and was not apparent at all in the grass field, where the turf protects the soil from the washing action of the rain.

The removal of the finest particles from the surface soil is attributed to deflocculation induced by the use of sodium nitrate and followed by the washing of the finest particles into the subsoil. This hypothesis is confirmed by chemical analysis of the "klays" separated in the mechanical analysis, by mechanical analysis of some of the subsoils, which were found to be richer in fine particles beneath the soils receiving nitrate, and by the condition of the same soils in the field, which showed every evidence of deflocculation.

DISCUSSION.

Dr. VOELCKER said that although he could not go so far as Mr. Hall in his estimation of the value of mechanical as against chemical analysis of soil, he nevertheless recognised the importance of the former and the advance which had been made with regard to it. It seemed, however, remarkable in the first paper that such similarity of composition was shown in the different separations formed by washing the soils.

In regard to the second paper, he could, from his own experiments on the Woburn soil—a light sandy one and very different to that at Rothamsted—quite bear out what had been noticed with respect to the action of sodium nitrate. On washing the former soil continuously with solutions of this salt, the finer portions of soil were carried down and the subsoil after a time became quite different in texture, forming a consolidated mass through which the water would not percolate. This was due, no doubt, as the author had indicated, to the carrying down of the finer particles. In this respect great differences were noted between the action of sodium nitrate and that of the sulphate and other salts of ammonium.

Dr. E. J. RUSSELL pointed out that what was really wanted was a knowledge of the total surface of the soil particles to a depth of say six inches; mechanical analysis gave very useful results but was not entirely satisfactory. There are some fundamental objections to the method; small particles from near the bottom of the column of liquid are deposited along with the larger particles which take the same time to travel from the top, and the deposit is therefore a mixture. Moreover, a disc-shaped particle will tend to place itself broadside on and be deposited simultaneously with a spherical particle of about the same sectional area. Consequently, it cannot be assumed that the particles have even approximately the same surface, although under the microscope the sediment may appear to be fairly homogeneous.

Mr. F. J. LLOYD said that the study of the physical nature of the soil had been neglected in England, whereas the remarkable researches of Whitney in America had shown that valuable information could be derived from this investigation. He regretted that the author had stated that the physical study yielded more important results than the chemical examination, because in his opinion the nature of the soil could only be discovered by the investigation of both its physical and chemical properties.

Mr. T. S. DYMOND pointed out that the method employed by the author involved the complete disintegration of the soil aggregates produced by years of cultivation. What information of value bearing on the proper treatment of

cultivated land could be obtained if the previous history of the soil were obliterated previous to analysis? More practical knowledge could be gained by the rough examination of the soil of a field with a spade than by the old methods of mechanical analysis. Would not this be still more true of the method now proposed?

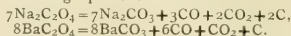
Dr. LUXMORE said that as the aim of mechanical analysis was to determine the structure of the soil it was needful in the first place to know the total quantity of the finest materials, which sometimes formed a layer over the coarser particles. If in addition to this a method could be derived by which the state of tilth could also be determined this would be a further advantage. One great benefit of the preliminary treatment with acid lay in the saving of time which it involved in a long and tedious process. From his own observations on the soils of Dorset he knew that the dissolved material other than calcium carbonate was very small in amount.

Mr. HALL, in reply, said that he would not attempt to consider the question raised by Dr. Voelcker and Mr. Lloyd as to the value of the mechanical analysis of a soil; the method, however, aimed at gauging the behaviour of a soil towards water, and the size of crops even in this humid climate was determined more by the amount of water available than by the soil constituents usually regarded as plant food. He agreed with Dr. Russell that the working surface of the soil particles was probably the factor of most importance, and one which could only be imperfectly deduced from the mechanical analysis. He did not, however, anticipate that it would be possible to estimate directly the behaviour of a soil in the field from any of the measurements they could obtain; the function of the mechanical analysis was rather to enable one to relegate a given soil to one or other of certain known types, the working qualities of which had been already ascertained by experience. This meant, then, the accumulation of the necessary data for a number of soils, and the first essential was to obtain a method which was so far accurate that it represented the permanent and not the accidental or temporary features of the soil.

*113. "The Decomposition of Oxalates by Heat." By ALEXANDER SCOTT.

In spite of the simple formulæ given to the oxalates, their decomposition by heat is by no means as simple as usually stated. Ordinary precipitated calcium oxalate turns grey on ignition, and this change, which is due to the separation of small quantities of carbon, occurs even with the purest calcium oxalate. This salt gives very little carbon dioxide and carbon, but always a little of each, decomposing practically in accordance with the equation usually given, $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}$.

Sodium and barium oxalates decompose in accordance with the following equations—

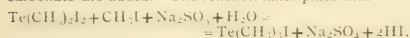


Magnesium oxalate gives exactly equal volumes of carbon dioxide and monoxide and no carbon, $\text{MgC}_2\text{O}_4 = \text{MgO} + \text{CO} + \text{CO}_2$, but almost all the other oxalates tested gave notable quantities of carbon dioxide and carbon.

*114. "Some Alkyl Derivatives of Sulphur, Selenium, and Tellurium." By ALEXANDER SCOTT.

When sulphur is heated at 180° with methyl iodide, 1 atom unites directly with 3 molecules of the iodide, forming the di-iodide of trimethyl-sulphine iodide, which is obtained as an almost black oil, but after this has been freed from excess of methyl iodide the solid, $\text{S}(\text{CH}_3)_2\text{I}_2$, may be obtained by dissolving the oil in ethyl acetate and precipitating by means of ether, when it separates in dark purple scales melting at 38° . Selenium behaves in an exactly similar way, the $\text{Se}(\text{CH}_3)_2\text{I}_2$ melting at 39° . To reduce these to trimethyl-sulphine and -selenetine iodides, water is added to their solutions in ethyl acetate and hydrogen sulphide is passed in until the liquid is colourless.

As Demarcay has shown, the action of methyl iodide on tellurium at 80° gives rise to tellurium dimethyl di-iodide, $\text{Te}(\text{CH}_3)_2\text{I}_2$, but this is not decomposed by heating to 180°, nor does it give a compound corresponding with those obtained from sulphur and selenium. To obtain tellurium trimethyl iodide, the di-iodide is dissolved in methyl iodide and equivalent quantities of sodium sulphite and sodium carbonate are added. The reaction takes place thus:—



the hydrogen iodide being then neutralised by the sodium carbonate. The tellurium trimethyl iodide is readily separated from the sodium salts by crystallisation.

The di-iodide of tellurium trimethyl iodide, produced by adding iodine to the iodide, is readily obtained in fine purple scales (m. p. 76·5°) by precipitation of its solution in ethyl acetate by means of ether.

Allyl iodide readily dissolves tellurium in the cold, giving an orange-coloured oil, from which the element is very readily obtained again. Ethyl iodide reacts in the same way as methyl iodide.

The author showed several reactions of tellurium dimethyl di-iodide and its derivatives.

*115. "The Ultra-violet Absorption Spectra of certain Enol-ketotautomers. Part I. Acetylacetone and Ethyl Acetoacetate." By EDWARD CHARLES CYRIL BALY and CECIL HENRY DESCH.

An attempt was made to determine the constitution of the metallic derivatives of acetylacetone and ethyl acetoacetate by means of their ultraviolet absorption spectra. The absorption spectra of alcoholic solutions of the aluminium, beryllium, and thorium derivatives of acetylacetone and the aluminium compound of ethyl acetoacetate were photographed, as well as those of the parent substances. Hartley and Huntingdon's method of experiment was adopted, but a different method of drawing the curves of absorption was employed. From a consideration of the absorption curves of acetylacetone and its metallic derivatives, it is evident that the constitution of these substances is very similar, as they all show a strong absorption band, the limits of which are very much the same in every case.

Ethyl acetoacetate, on the other hand, shows no absorption band, whilst its aluminium derivative shows a strong band almost identical with those of the acetylacetone group.

These results appeared at first to indicate that acetylacetone and its derivatives and the aluminium compound of ethyl acetoacetate had the enolic formula, and suggested the keto-formula for ethyl acetoacetate itself. This view was not upheld by the study of the spectra of ethyl ethyl-acetoacetate, and its isomeride, ethyl β -ethoxycrotonate; in both cases, only continuous absorption was obtained without any band at all. The band therefore cannot be characteristic of either the enolic or the keto-modification, but appears to be due entirely to the dynamic isomerism between the two forms. Experiments were made to test this by observing the action of sodium hydroxide or hydrochloric acid, which should materially alter either the size or the persistence of the absorption band; the former reagent should increase it, and the latter decrease it owing to their accelerating and retarding influence respectively on the dynamic isomerism. It was found that a very small amount (1 equivalent) of sodium hydroxide produced a band in the absorption spectrum of ethyl acetoacetate, this band being increased by the addition of more alkali until with excess it was larger and more persistent than that given by the aluminium derivative. Hydrochloric acid was found to have a marked action in decreasing the absorption of ethyl acetoacetate; its action was better observed in the case of ethyl β -aminocrotonate, when it was found that the absorption band was decreased more and more by repeated addition of small quantities of the acid.

The conclusion is therefore drawn that with acetylacetone, ethyl acetoacetate, and their metallic derivatives, a

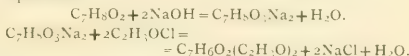
state of dynamic isomerism exists in the solution; that the presence of the band in their absorption spectra is due to this isomerism, and that its persistence is a measure of the number of molecules in the state of vibration. It would thus appear that the absorption band is a method of measuring the amount of reaction taking place between two isomeric substances which are in equilibrium.

*116. "The Action of Acetyl Chloride on the Sodium Salt of Diacetylacetone and the Constitution of Pyrone Compounds." By JOHN NORMAN COLLIE.

The action of acetyl chloride on the sodium salt of diacetylacetone was investigated with the object of determining whether the introduction of two acetyl groups into dimethylpyrone would destroy its property of forming salts with acids.

As a result of the action of acetyl chloride dissolved in chloroform on the sodium salt, a compound melting at 124° was obtained, which was undoubtedly diacetyldimethylpyrone (compare Thomas and Lefevre, *Bull. Soc. Chim.*, 1888, 1, 103—194). On repeating this operation, the chief substance produced melted at 95·4°, whilst in another experiment, in which the substances were allowed to react at the temperature of a freezing mixture, a compound melting at 75° was obtained.

These three substances were isomeric, having the formula $\text{C}_{11}\text{H}_{12}\text{O}_4$, and were produced according to the equations:—



(1) Diacetyldimethylpyrone gave no coloration with ferric chloride, and could be sublimed; when boiled with barium hydroxide solution, a yellow barium salt was produced, which dissolved in dilute hydrochloric acid and gave a deep red coloration with ferric salts. Bromine was not decolorised by it. The original substance was totally devoid of any basic properties, and gave neither a hydrochloride nor a platinumchloride.

(2) The compound melting at 95° gave a purple coloration with ferric chloride solution, and the orcinol reaction with chloroform and caustic soda. When heated with 80 per cent sulphuric acid, acetic acid and orcinol were obtained; it gave, with bromine, a monobromo-derivative, $(\text{C}_{11}\text{H}_{11}\text{O}_4\text{Br})$ (m. p. 79°), and, with acetic anhydride, a monoacetyl derivative, $\text{C}_{11}\text{H}_{11}(\text{C}_2\text{H}_3\text{O})\text{O}_4$ (m. p. 75°). It dissolves in aqueous soda with a yellow colour, and, after boiling, can be re-precipitated unchanged on the addition of an acid; it is, therefore, diacetylorsinol.

(3) The third substance (m. p. 75°) also gave a purple-red coloration with ferric chloride; it decolorised a solution of bromine in the cold, and, after heating for some time, gave the orcinol reaction with caustic soda and chloroform, but, on warming with this alkali, it also was transformed into the compound melting at 94°, whilst with hydrochloric acid it changed into diacetyldimethylpyrone (m. p. 124°). These curious transformations received scanty explanation from the accepted molecular constitution of dimethylpyrone, and formulae for pyrone and its derivatives were brought forward with the view of explaining the foregoing transformation.

*117. "Our Present Knowledge of the Chemistry of Indigo." By WILLIAM POPPLEWELL BLOMAM.

As the determination of the maximum amount of indigo obtainable at each successive stage of its preparation ("mahai") and of the quantity present in the leaf of the green plant depends on the purity of the indigotin employed as a standard, the author has estimated the percentage of nitrogen in the best specimens procurable, and has thus found that they contain only about 90 per cent of indigotin.

Since the pure substances could not be prepared by the action of solvents on cake indigo or the synthetical product, the crude indigo was sublimed under diminished pressure, and in this way a well crystallised product was

readily obtained which gave the percentage of nitrogen required for indigotin.

This pure material when sulphonated and subjected to analysis by the permanganate method was found to give values ranging up to 300 per cent of the weight of substance taken. As this method is used in ordinary technical analyses of indigo, this result explained the extraordinary variations observed in the published values given for cake indigo and the products obtained during the successive stages of the manufacture ("mahai").

It has also been found that the red substance occurring in the cake obtained from plant-indigo and known as "indirubin" or indigo-red, is not, as stated, a derivative of indigo, as it contains no nitrogen. This material, which may consist of a mixture of compounds, will be further investigated.

118. $\Delta^1:3:4$ "Dihydrobenzene." By ARTHUR WILLIAM CROSSLEY.

Dibromotetrahydrobenzene, prepared by Bayer's method (*Annalen*, 1894, cclxxviii., 88), is a colourless, highly refractive liquid, boiling at $116-117^\circ/29$ m.m. When treated with concentrated alcoholic potassium hydroxide, it yields a small quantity of $\Delta^1:3$ -dihydrobenzene, but principally the ethyl ether, $C_6H_5 \cdot O \cdot C_2H_5$, of hydroxytetrahydrobenzene as a colourless liquid boiling at 155° , and possessing a pungent odour of peppermint.

Quinoline removes two molecules of hydrogen bromide from dibromotetrahydrobenzene, giving $\Delta^1:3$ -dihydrobenzene, which boils at $81.5-82^\circ/767$ m.m., and, like the dihydrobenzene obtained from dihydroresorcin (Crossley and Haas, *Trans.*, 1903, lxxxiii., 494), is characterised by only adding on two atoms of bromine to form 1:4-dibromo- Δ^1 -tetrahydrobenzene melting at 104.5° , and decomposing with evolution of hydrogen bromide at 170° . That this substance is in reality a dibromotetrahydrobenzene is proved by the fact that on treatment with quinoline it loses two molecules of hydrogen bromide with formation of benzene.

119. "The Absorption Spectrum of *p*-Nitrosodimethylaniline." By WALTER NOEL HARTLEY.

It was pointed out that the usual formula assigned to benzoquinone is less consistent with its chemical properties as an oxidiser than the peroxide formula, and that an un-reduced benzene ring is in accord with the optical properties of the substance, since its spectrum exhibits powerful absorption bands. The usual formula, on the other hand, contains the partially reduced carbon ring present in hydro-aromatic substances, and the spectra of these are characterised by an absence of absorption bands. The absorption bands in the ultra-violet are always associated with the production of colours, even when the substance examined shows no visible colour, and such substances are in reality chromogens (*Trans.*, 1887, li., 154-202). Nitroso-compounds of the aromatic series have a powerful and extensive selective absorption in the ultra-violet, and it was thought possible to draw a distinction between these and the closely related oximes.

The following conclusions were deduced:—1. The absorption caused by *p*-nitrosodimethylaniline at the less refrangible end extends into the infra-red, and at the more refrangible far into the ultra-violet. The transmitted rays are thus restricted to a band of yellow and green light bordered on either side by a band of intense absorption.

2. There appears to be a decided difference in constitution as judged by their spectra between *p*-nitrosophenol or quinoneoxime and *p*-nitrosodimethylaniline which cannot be accounted for by a substitution of hydroxyl for the group $N(CH_3)_2$.

3. The alkyl substituted phenols and anilines absorb varying quantities of the ultra-violet, the absorption not extending into the visible spectrum, but the introduction of the NO , as distinguished from the NOH group, extends the absorption far into the coloured rays. This appears to be a characteristic effect of the nitrosyl group in conjunction with the benzene ring.

4. Although the absorption of rays in the blue and violet by *p*-nitrosodimethylaniline is strong, there is at a certain dilution a transmission of the greater part of the ultra-violet.

This explains the action of Wood's screen, which cuts off the visible rays while it transmits some of the ultra-violet. On testing the solutions of *p*-nitrosodimethylaniline, it was found that some red rays were still transmitted, but it is quite possible to adjust the thickness of the solutions so that with a quartz lens and electric light what appears to be perfect darkness causes the fluorescence of uranium nitrate and barium platinocyanide. The appearance of the crystals was brightest when some obscure or feeble blue rays were transmitted.

From a consideration of the facts referred to in connection with conclusion 3, and the previous observations on benzoquinone and its oxime, dioxide, chloroimide, and dichloroimide, it appears to be not improbable that a solution of *p*-nitrosophenol is a mixture of two tautomeric forms, the one a phenol and the other an oxime.

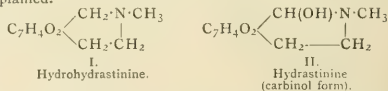
120. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part VI. The Relationship between Solution-volume and Rotation of the Dialkyl and Potassium Alkyl Tartrates in Aqueous Solution." By THOMAS STEWART PATTERSON.

Values for the molecular solution-volumes of dimethyl-, diethyl-, di-*n*-propyl, potassium methyl-, potassium ethyl-, and potassium *n*-propyltartrates are given, and the changes of volume due to solution in water compared with the corresponding changes in rotation. It is shown that in both series a contraction of 1 c.c. per gram-molecule produces the greatest change of rotation in the methyl and the least change of rotation in the *n*-propyl ester, and that the perplexing rotation changes of these compounds, due to solution in water, can at least be brought into harmony when a casual connection between solution-volume and rotation is assumed.

121. "The Constitution of Hydrastinine." By JAMES JOHNSTON DOBBIE AND CHARLES KENNETH TINKLER.

The study of the absorption spectra of hydrastinine, $C_{17}H_{15}O_2N$, has yielded results precisely similar to those obtained with cotarnine (*Trans.*, 1903, lxxxiii., 598).

Solutions of hydrastinine in ether or chloroform, as like the solid substance, colourless, and their absorption spectra are practically identical with the spectra of hydrohydrastinine, a compound which is generally considered to have the constitution represented by formula I. From this it is argued that the carbinol formula II, which represents hydrastinine as differing from hydrohydrastinine only in the replacement of an atom of hydrogen by a hydroxyl group, should be preferred to the open-chain or aldehydic formula of Roser, which would leave the agreement between the absorption spectra of the two substances entirely unexplained.



On the other hand, the aqueous or alcoholic solutions of hydrastinine, which are yellow and fluorescent, give spectra which agree with those of the hydrastinine salts. It would therefore appear that, under the influence of these solvents, hydrastinine changes from the carbinol to the ammonium base, the hydroxyl group shifting from the carbon atom to the nitrogen and forming the complex $>N(CH_3) \cdot OH$.

The spectra of the colourless solutions agree closely with those of the corresponding solutions of cotarnine. The spectra of the coloured solutions possess three absorption bands corresponding in position with two bands in the cotarnine spectra.

All the hydrastinine derivatives examined give spectra

which are identical or nearly so with those of hydrohydrastinine or of the hydrastinine salts.

Alcohol imparts a yellow colour to an ethereal solution of hydrastinine, the depth of colour increasing as the proportion of alcohol to ether is increased. An examination of the spectra of such solutions shows that as alcohol is gradually added the carbinol form changes into the ammonium base form. The opposite change is brought about by the addition of alkalis to the yellow solution of hydrastinine compounds, the disappearance of the fluorescence marking the complete conversion of the ammonium base form into the carbinol form.

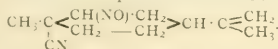
122. "The Influence of Moist Alcohol and Ethyl Chloride on the Boiling Point of Chloroform." By JOHN WADE and HORACE FINNEMORE.

Chloroform, when made from alcohol, contains a small quantity of ethyl chloride, the absence of which from chloroform made from acetone detracts from its efficiency as an anæsthetic. The ethyl chloride depresses the boiling point of the chloroform; it was partially isolated by fractionation through a Young's evaporator column, and was identified by conversion into silver propionate.

Incidentally, the authors have isolated binary mixtures of chloroform and alcohol, chloroform and water, and a ternary mixture of chloroform, alcohol, and water, all of minimum boiling point. The first binary mixture boils at 59.4°/760 m.m., has a sp. gr. 1.4125 at 15°/15°, and contains 7 per cent of alcohol. The second binary mixture boils at 56.1°/760 m.m., and contains about 1 per cent of water. The ternary mixture boils at 55.5°/760 m.m., and contains 4 per cent of alcohol and about 3.5 per cent of water. The water in both these mixtures separates at once from the distillate.

123. "Limonene Nitrosocyanides." By WILLIAM AUGUSTUS TILDEN and FREDERICK PEACOCK LEACH.

The nitrosocyanide referred to (*Proc.*, 1902, xviii., 163) by Tilden and Burrows as a liquid is found to be a crystalline, optically active solid, m. p. 90—91°, and $[\alpha]_D + 165^\circ$; it yields a benzoyl derivative, which crystallises in shining plates melting at 107°. The nitrosocyanide has a monomolecular structure, $C_{10}H_{16}NO \cdot CN$, and the formula for limonene having been recently established by Perkin, the nitrosocyanide must be represented as follows:—



This compound is obtained by digesting limonene β -nitrosocyanide with potassium cyanide. It is also the chief product of the same treatment of the mixed α - and β -nitrosocyanides. It has not yet been obtained from pure α -nitrosocyanide, which yields a viscid product, but from the latter a benzoyl compound is obtained, which is identical with the benzoyl derivative of the β -nitrosocyanide. The investigation will be continued.

124. "Photochemically Active Chlorine." II. (A Preliminary Notice). By CHARLES HUTCHINS BURGESS and DAVID LEONARD CHAPMAN.

A considerable number of experiments have now been performed with the purpose of discovering the conditions under which the activity of chlorine gas or its solution is induced and destroyed (*Proc.*, vol. xx., p. 52), the following being a brief summary of some of the results obtained:—

(1) Active chlorine is formed by the action of light or heat on inactive chlorine. (2) Moist chlorine, when heated to the boiling point of water and then cooled to the ordinary temperature, is rendered almost as active as by the action of light. (3) By the passage of the electric discharge through inactive chlorine (compare J. W. Mellor, *Proc.*, vol. xx., p. 140).

It has also been shown that freshly prepared electrolytic gas and chlorine are almost at their maximum activity, and in measuring the activity of either of these gases it is very necessary to make sure that the chlorine contained in the control actinometer is inactive.

It has now been observed that aqueous solutions of certain acids and salts are more effective in removing the activity than pure water.

An active solution of chlorine in water can be prepared either by leaving the liquid in contact with active chlorine or by heating aqueous solutions of chlorine.

Only a very small fraction of the activity is removed by pumping the chlorine out of an active solution under diminished pressure, and when an active solution is distilled in a vacuum both the distillate and the residual liquid are active. Aqueous solutions of chlorides through which ozone has been passed are more active than solutions of the same strength which have not been thus treated.

The residual liquid remaining after removing the chlorine under diminished pressure, when treated successively with potassium iodide and N to thiosulphate, still retains a large proportion of its activity.

The condition of the moist chlorine having been found to be the cause of the induction period, experiments were made for the purpose of deciding whether this phenomenon is due to the formation of a compound of the type $Cl_2 \cdot H_2O$, which is subsequently destroyed by hydrogen with the formation of hydrochloric acid. Comparative measurements of the induction period and of the rate of formation of hydrochloric acid after the induction period were made, and on applying the law of mass action to the results it was seen that if the foregoing assumption is correct, then at least one-half of the chlorine in the actinometer must have been converted into the compound $Cl_2 \cdot H_2O$ before hydrochloric acid began to be formed in appreciable quantity, a result which is obviously absurd.

The conditions of formation of active chlorine precisely correspond with those which are known to be necessary for the substitution of hydrogen in the side chain of a benzene compound.

125. "Additive Compounds of Anhydrous Magnesium Bromide with Organic Oxygen and Nitrogen Compounds." By JOHN JOSEPH SUDBROUGH, HAROLD HIBBERT, and STANLEY H. BEARD.



by the action of a dry ethereal solution of ethylene dibromide on ethyl succinate in the presence of dry magnesium, an additive compound of magnesium bromide and ethyl succinate was obtained. This is an extremely hygroscopic, crystalline solid, which may readily be prepared by the direct union of its components; it has the composition $(CH_2 \cdot CO_2Et)_2 \cdot MgBr_2$.

Additive products of other organic oxygen compounds, such as ether, amyl ether, benzaldehyde, cinnamaldehyde, benzophenone, pyruvic acid, and ethyl benzoate, have been obtained. Amines and nitrites appear to be capable of forming similar additive compounds, whereas hydrocarbons are not.

The compounds are all extremely hygroscopic and difficult to obtain quite pure.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, June 24th, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A PAPER on "Chemical Dissociation and Electrical Conductivity," by A. E. GARRETT and Dr. R. S. WILLOWS, was read by Dr. WILLOWS.

It has been shown by Beattie (*Phil. Mag.*, 1899) that a mixture of salt and iodine, when placed on a zinc plate and heated, gives rise to electrical conductivity, although separately no such effect is produced. This is shown to be due to the formation of zinc iodide. Following on this the

electrical conductivity produced by heating various salts is investigated under different conditions of temperature and electric field. A large excess of positive electricity is found in nearly every case.

Mr. SKINNER expressed his interest in the paper, and pointed out that the chief leak did not begin until the iodine was completely vaporised. He asked if the ions were produced in the mixture or in the gas. Had the authors tried the effect of screening the mixture from the electroscope?

Dr. C. CHREE remarked on the fact that the authors employed formulæ of the type $I = at^n$, t representing absolute temperature, under circumstances in which n was a large positive number, in one case as big as 100. To fit such a formula I must be practically either infinitely small or infinitely large, except over a very limited range of temperature. He should like some further details as to the method of arriving at formulæ of a type so remarkable physically, and as to the range of temperature wherein they were supposed to hold.

Dr. WILLOWS, replying to Mr. Skinner, said that the effect was still produced when the mixture was covered with a metal plate, but they had not tried screening with mica. In reply to Dr. Chree, he said that their formula held over a range of 100° C., and that Dr. H. A. Wilson had arrived at a similar formula which applied over a range from 200° C. to 1000° C.

A paper on "The Magnetisation of Iron in Bulk" was read by Dr. W. M. THORNTON.

The paper is in three sections. The first describes a method of measuring large quantities of magnetism by the use of an exploring coil placed around the core and an exciting coil in series with a recording milli-voltmeter. This was applied to determine the complete loops of magnetisation for two rings of cast steel and cast iron weighing respectively 3 and 6 cwt. The results were checked by a quantometer. The second section deals with the curves of rise of magnetising currents, when the core is solid and when laminated, as affected by the reaction of the core-currents, and also by the change of permeability during magnetisation. A second simple method is given of measuring large quantities of magnetism in circuits having a large time constant, suitable for testing dynamo-electric machines. From two curves of rise, with the current in one reversed, expressions are given for finding the total induction in the core and its ratio to the residual magnetism. In the last section an example is given of the sudden dip in the curve of rise observed only with large cores. The growth of current in a coil surrounding a solid circular core is calculated by Heaviside's formula, assuming constant permeability. No dip is found in the calculated curve, and it is therefore caused by a brief magnetic impulse which corresponds to the slip of the molecules at saturation seen in Ewing's model of the magnetisation of iron. Photographs are given showing the direction of flow of eddy currents in cores of rectangular section of proportions 1:1, 1:5:1, and 2:1.

Prof. S. F. THOMPSON expressed his interest in the paper, and referring to the curves showing the rise of the magnetising current, said he thought the explanation given by the author was not the only possible one. He was not inclined to think that the effect was due to internal eddy currents in the core. The fact that the growth of the magnetisation current was irregular was well exhibited in separately excited dynamos with large field magnets, where the effect could be easily seen in the movements of the amperemeter needle. In the author's curves showing the rise of the quantity of magnetism in a circuit with the current, first with the current direct and then with it reversed, he pointed out that a difference would be expected because the core would not be in the same magnetic condition at the beginning of the two experiments.

Mr. W. H. PRETTY said that the question of magnetisation tests of iron and steel in bulk was a very important one. The curves shown by the author suggest the possibility of detecting cavities in steel castings, as such castings

would doubtless give curves differing from those representing a truly solid block of the same material cast at the same time and subjected to the same after-treatment. It would be interesting to have a series of tests on the same block of steel, say, in which each process in the manufacture is represented, i.e., as cast after annealing, and after the surface-scale or skin has been removed to various depths; also after the block has been cut up into slabs or laminæ and put together again. Referring to the dip in the curves of rise of magnetisation observed with large cores, Mr. Pretty said it was not unlikely due to internal mechanical stress and the accompanying strain, and that as it became possible to obtain steel more and more homogeneous such internal molecular changes would become more apparent.

Dr. THORNTON, in reply to Mr. Pretty, said that he was now experimenting upon the effect of cutting up a large core into laminæ and then building up the core again.

NOTICES OF BOOKS

Chemical Novelties for 1904. ("Les Nouveautés Chimiques pour 1904"). By C. POULENC. With 185 illustrations in the Text. J. B. Baillière et fils. 1904. Pp. 352.

THE author has kept to the same plan as in former years. The first chapter deals with chemico-physical apparatus, such as those for the determination of densities, of high temperatures, &c., and a sub-division has been introduced in this chapter for apparatus for the liquefaction of gases by M. Olszewski's methods, by which means these operations have been made more and more practicable, and the returns considerably increased.

In the second chapter we find apparatus for chemical manipulation proper, by which long and difficult operations are much simplified. Among the apparatus for the preparation and purification of gases, we may call special attention to the new one devised by M. Moissan, in which he makes use of the low temperatures given by liquid air, carbonic acid, or oxygen, &c.

Chapter III. deals with electrical apparatus in general, and Chapter IV. with that specially used in analysis.

F. Jean has devised a new and practicable piece of apparatus for the determination of the carbonic oxide and carbonic acid in inhabited places; while among those instruments used for the detection and estimation of arsenic we may call attention to that brought out by E. Bonjean for the detection of this metalloid in pharmaceutical products, and that of G. Bertrand for effecting the same object in animal tissues.

In the fifth and last chapter we find some of the latest apparatus used in the study of bacteriology.

Twenty-eighth Annual Report of His Majesty's Inspectors of Explosives; being their Annual Report for the Year 1903. London: Darling and Sons, Limited. 1904. Pp. 236.

It is satisfactory to read that the inspectors have found no reason to complain of any falling off in the general condition of factories and magazines, and in one instance only have they had occasion to institute legal proceedings for any irregularity, while the occupiers of factories and magazines have invariably shown perfect readiness to remedy such defects as have been pointed out.

The number of deaths from accidents by fire or explosion in the manufacture of explosives is 5, and is below the average for the decade, viz., 6.4. This death-rate cannot be called excessive, and will compare favourably with the death-rate in other dangerous trades.

The total number of factories under continuing certificate or license is 147, being a reduction of 3 during the year.

Four factories have become extinct during the year, and one new one has been confirmed, while there are seven

applications outstanding. Several cases of illegal manufacture of blasting cartridges by miners in their houses were brought to light by accidents during the year. It is to be regretted that, notwithstanding the vigilance of the police, this practice still prevails in certain districts.

In consequence of the accident which occurred at Waltham Abbey in December, 1902, the inspectors considered it advisable to impose further restrictions on the manufacture of cordite M.D. After full discussion with representatives of all the manufacturing firms interested, and of the War Department and War Office Explosives Committee, the character of the restrictions was settled, and these have been embodied now in the licenses of the factories concerned.

During the year, 244 visits have been made to factories, which now number 147, all having been visited at least once, while 476 visits have been made to magazines; in very few instances have serious defects or irregularities been found.

No proceedings for illegal storage have been instituted during the year.

The amount of foreign blasting explosives containing nitroglycerin imported during 1903 was 2,330,582 lbs. against 1,830,277 lbs. in 1902. The corresponding figures for blasting explosives not containing nitroglycerin are 168 lbs. and 2 cases for 1903, against 12,000 lbs. in 1902.

CORRESPONDENCE.

WILLIAMSON'S THEORY OF ETHERIFICATION.

To the Editor of the Chemical News.

SIR,—In the interest of accuracy it seems proper, now that Prof. Williamson is no longer living, to call attention to an error which appears in the latest edition of such a widely used text-book as Richter's "Organic Chemistry," both in the original German and in the American translation (vol. i., p. 134). There it states that Chancel preceded Williamson in publication. The facts are quite otherwise, for Chancel writes most explicitly (*Comptes Rendus*, 1850, xxxi., 521) that he was prompted to immediate publication by the appearance of Williamson's paper, "sans vouloir en aucune façon, faire une réclamation de priorité."

The mistake has doubtless arisen from the fact that although Williamson read his paper before the British Association on August 3, 1850, it was not really published in this country until the November following (*Phil. Mag.*, 1850, [3], 37, 350), whereas Chancel's paper appeared in October. The "British Association Report" (Edinburgh Meeting, 1850, p. 65) contains an abstract, but was not issued until 1851, and the oft-quoted reprint in the *Quarterly Journal of the Chemical Society* did not appear until 1852. On the continent, however, he fared better, the full paper being included in the September number of the *Comptes Rendus des Travaux de Chimie* of MM. Laurent and Gerhardt, to which Chancel refers, two months before its publication in England!—I am, &c.,

F. SOUTHERDEN.

Technical College, Finsbury, E.C.,
July 1, 1904.

PTOMAIN POISONING.

To the Editor of the Chemical News.

SIR,—Having regard to the frequency of cases of ptomaine poisoning through eating canned goods, perhaps you will be able to find room in your paper for one possible explanation of such cases.

A very large proportion of the tinman's solder used nowadays contains 2 or 3 per cent of antimony as an impurity, and it seems possible that the presence of this metal as an impurity may cause electrochemical changes to be set up in the meat or fruit juices, resulting in corrosion of the

solder and consequent production of a line of more or less porous solder, allowing of the infiltration of air laden with micro-organisms capable of establishing a toxic metabolism. I am, &c.,

SIGMA.

MAGNESIA CUPELS.

To the Editor of the Chemical News.

SIR,—Your readers may perhaps like to hear the opinion of an assayer of fifty-five years' experience with regard to magnesia cupels.

I have made numerous experiments with all the known makes, including those supplied by my own firm, and while I am ready to admit that for assays which yield only a minute bead of metal, they are as good as bone-ash (not better), they are unsuitable for those yielding large metallic beads, such as bullion assays; the reason being that the said assays are made uncertain by the large (but variable) quantity of magnesia adhering to the base of the beads so persistently that it cannot be completely cleaned off; this does not, however, occur with well-made bone-ash cupels.

The consumption of bone-ash cupels in my laboratory is over 100,000 a year, so I can speak with some confidence in the matter.—I am, &c.,

A CONSTANT READER.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 23, June 6, 1904.

Method of continuous Recording of the Ionisation of Gases. The Ionograph.—Ch. Nordmann.—The author describes a method by which automatic measurements of ionisation of gases may be taken. The apparatus employed causes a photographic record to be given, by which immediate readings can be taken at any moment without the intervention of further operations when once the apparatus has been started and regulated. The apparatus can be employed for various researches on ionisation and radio-activity.

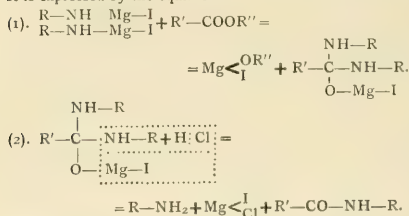
Influence of Frequency on Electrolysis by means of Alternating Currents.—André Brochet and Joseph Petit.—Up to the present time it has always been admitted that during electrolysis by means of an alternating current frequency has a considerable action on the reactions brought into play, and that the quantity of the products deposited at the electrodes decreases rapidly proportionately as this frequency rises. During the present series of researches the authors prove that this fact is not general, and that frequency has only a very slight action in the case of the particular reactions due to the alternating current, such as the solution of iron and platinum in potassium cyanide or that of lead in sulphuric acid. In the case of nickel and cobalt, frequency acts in a very peculiar manner, quite contrary to that already admitted. As a final result of their investigations the authors state that alternating currents appear to possess electrolytic qualities quite different from those of continuous currents.

Use of N-rose in Chemistry.—H. Becquerel.—Already inserted.

Reduction of o-Nitrobenzylic Alcohol. General remarks on the Formation of Indazylic derivatives.—P. Freundler.—The anomalies which are noticed during the alkaline reduction of the ortho-substituted nitrated derivatives are apparent in a well-defined way in the case of o-nitrobenzylic alcohol. The author shows that this

atter substance does not give the azoic compound when subjected to the action of powdered zinc in presence of alcoholic soda. An investigation on the subject of azoic compounds with ortho-substituted alcohol function leads to a very simple explanation of this fact.

New Method of Preparation of Anilides.—F. Bodroux.—The primary amines react on organo-magnesium compounds in the following manner:— $R-NH_2 + R'-Mg-I = R'H + R-NH-Mg-I$. M. Jot-sitch synthesised acetylenic alcohols and acids from the magnesium compounds of acetylenic carbides which are formed by an analogous mechanism. The author utilises these products of substitution of the amines to introduce the group $R-NH$ into the organic molecule. Carbonic anhydride is apparently without action on these compounds, $R-NH-Mg-I$, but the same is not the case with the ether salts of the monobasic acids. The reaction which the author studies is that of the primary aromatic amines, causing the formation of the corresponding anilides only. It is expressed by the equation:—



MISCELLANEOUS.

Corbin and Stewart's Handbook of Physics and Chemistry.—Messrs. J. and A. Churchill have the pleasure to announce that a section on Light has now been added to the second edition of this work. This subject was originally omitted because, when the new edition was put in hand, it was not included in the curriculum. The new section contains twenty-five illustrations. The book is still published at 6s. 6d.

Kelly's Directory of Chemists and Druggists, 1904.—The tenth edition of this useful Directory has just been published. It includes manufacturing chemists, wholesale druggists, dysalsters, and all other trades connected therewith in England, Scotland, and Wales, and the principal towns in Ireland, the Channel Islands, and the Isle of Man. In the pages of this book will be found the names of over 56,000 persons, being an increase of about 4000 over the last edition. Besides the trade headings, this Directory also includes the more scientific branches, such as analytical and metallurgical chemists, members of the Pharmaceutical Society, and others whose scientific researches are constantly developing important results.

Livingstone College Year-book.—This Year-book contains hints to travellers in matters of health, outfit, and travel, and is published by the Travellers' Health Bureau, Livingstone College, Leyton, E. A special feature of the Year-book on this occasion is a short statement of the risks to health in a tropical climate and the best means of meeting them. This is the first time that such hints have been issued from Livingstone College in a concise form, and it is hoped that later on they will be amplified and form a short guide to health in the tropics. During the past year excellent work has been done in the department of research in tropical medicine, and one by one the great disease scourges of the tropics are being traced to their cause, and are found to be preventable; such work as this deserves every encouragement, and we feel confident that Livingstone College will justify its foundation.

RADIUM

ON SALE AND LET ON HIRE.—Write for terms.

The following can be had by return of post.

Pitchblende, direct from Joachimsthal, very radio-active, from 1/- to 30/- per piece.
Itacolomite, or flexible sandstone, 10/- to 25/- per piece (very rare).
Kunzite, 1/- per gramme. Selected, clear, 2/-
Spartite (see NATURE, 31/3/04, fol. 523), 2/- and upwards.
Chlorophane, 2/- and upwards. Barium Platino Cyanide in large Crystals in course of manufacture. (ORDERS BOOKED).
Zinc Sulphide. Phosphorescing a beautiful Green, 2/6 per tube.
" " " " Yellow, 2/6
Calcium Sulphide " " Violet, 1/-
Radio-active Residue from which Radium is made; very scarce, 2/- tube.
Polonium Sulphide, in tubes of one gramme, 21/-
" on Bismuth Rod or Disc, ... 25/-
" on Copper " ... 25/-
Radio-active Screens (Willemite), 6d. per sq. inch. Plat. Bar. Cyan. Screen, 9d. sq. inch.
" " (Zinc Sulph.), 10 x 10 cm. 7/6.

Professional Men, Universities, Schools, &c., allowed special terms

Our newly invented Thorium Inhalers may be had on hire.

ARMBRECHT, NELSON & CO.,
71 & 73 DUKE ST., GROSVENOR SQ., LONDON, W.

Telephone: GERRARD 4942.

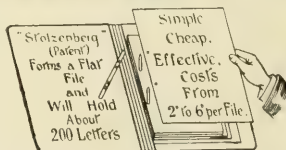
N.B.—We have to-day received a consignment of the New Zealand Vegetable Caterpillar: it is from 2 to 3 inches long, with a stem showing fructification growing out of its head. Scientific name of the insect is *Hepialus virescens*; the name of the fungus is *Sphaeria Robertiana*. Specimens may be had from 10/6 to 21/-, according to quality and size. TERMS CASH WITH ORDER.

Goods may be returned if not approved of, when money will be refunded.

Perfect Order amongst your
Scientific Papers,
Research Records, &c.,

IS SECURED BY THE

"STOLZENBERG"
SYSTEM OF FILING.



The "Unit" of the System is a simple flat File, made in six distinct colours, for classifying under Subjects, &c.

Used by SIR WILLIAM CROOKES, LORD KELVIN, Royal Commission on Tuberculosis, Baden Aniline Works (50,000), and by thousands of private persons as well as Business Concerns.

Satisfaction guaranteed; otherwise goods taken back and money returned.

Sample Set, consisting of 12 best Files, 4to and fcap., with strong nickel-plated Perforator, and Patent Lifter, packed in leather-board box, 10/6 post free.

THE STOLZENBERG PATENT FILE CO.,
50, Bishopsgate St. Without, London, E.C.

THE CHEMICAL NEWS.

VOL. XC., No. 2329.

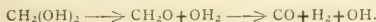
THE RETARDATION OF COMBUSTION BY OXYGEN.*

By HENRY E. ARMSTRONG, Ph.D., F.R.S.

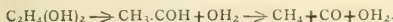
IN the course of his researches on gaseous explosions, H. B. Dixon has laid stress on the fact that carbon monoxide, rather than the dioxide, is the initial product of the combustion of carbon and of its gaseous compounds; moreover, he has shown that water plays a peculiar and all-important part in the combustion of the monoxide; and he has proved, in a number of cases, that oxygen is by far the most effective diluent in retarding combustion. These, in some respects, paradoxical conclusions have not yet been sufficiently explained. Recent researches† emanating from the Manchester school have brought new facts to light, however, which have an important bearing on the interpretation of explosive changes—so much so, indeed, that it is no longer difficult to paint a consistent and fairly complete picture of the mechanism of combustion. (Compare H. E. Armstrong, "The Mechanism of Combustion," *Trans. Chem. Soc.*, 1903, vol. lxxxiii., p. 1088).

1. It would seem that, in the case of hydrocarbons, there is no preferential combustion either of hydrogen or of carbon: initially, the hydrocarbon merely undergoes hydroxylation. As hydroxylation proceeds more readily when it has once taken place—owing to the attraction of oxygen for oxygen—the first product may easily escape observation; thus, Bone and Wheeler were unable to detect the formation of hydroxymethane (methyl alcohol) from methane; Bone and Stockings, however, succeeded in obtaining ethyl alcohol, C_2H_5OH , from ethane, C_2H_6 .

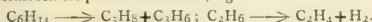
2. A stage in the hydroxylation is soon reached when the thermochisms begin to take place. Thus, dihydroxymethane breaks up as soon as it is formed into water and formaldehyde, which is in turn easily resolved into hydrogen and carbon monoxide:—



Dihydroxyethane, in like manner, gives rise to acetaldehyde, which, under some conditions, breaks up into methane and carbon monoxide:—



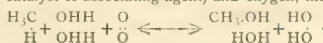
3. It is to be supposed that the more complex hydrocarbons are, to a large extent, resolved into simpler thermochisms prior to oxidation, e.g.,—



The change may extend even to the formation of carbon, when a relatively small proportion of oxygen is present. In high temperature changes (explosions), such thermochisms probably play an all-important part.

4. The precise manner in which oxygen is introduced into the hydrocarbon molecule is a matter of some interest. If oxygen molecules were directly active as wholes and the actual, immediate and sole cause of the oxidation, there would seem to be no reason why the dihydroxy-derivative should not be directly produced rather than the monohydroxy; the observation made by Bone and Stockings, that ethyl alcohol is producible from ethane, therefore, is of crucial importance. But on general grounds, regarding the change as electrolytic in character, it is probable that the electrolyte, i.e., conducting water, is the immediate

source of the oxygen; and that the oxygen molecule* plays the part of depolariser. From the same point of view, it appears probable that the water molecules contribute hydroxyl rather than oxygen. The process may be formulated as involving the conjugation of hydrocarbon (probably through its carbon) with water (acting primarily as the catalyst or associating agent) and oxygen, thus:—



5. According to the view here advocated, carbon dioxide is necessarily a later product of change than the monoxide—in fact, the final product. It is to be supposed that, in its formation from the monoxide, the latter is first converted into formic acid. On this assumption, it is easy to understand that the presence of so large a proportion of water is required in order that the explosive wave may attain to its greatest velocity, as the affinity of water for carbon monoxide is relatively slight, and the reversible change one which takes place mainly in the direction:—



The figures given by Dixon are as follows (*Phil. Trans.*, A, 1893, vol. clxxxix., p. 97):—

Condition of mixture.	Per cent of steam present.	Mean rate in metres per second.
Well dried	—	1264
Dried	—	1305
Saturated at 10° C.	1.2	1676
" 20	2.3	1703
" 28	3.7	1713
" 35	5.6	1738
" 45	9.5	1693
" 55	15.6	1666
" 65	24.9	1526
" 75	38.4	1266

The gradual retardation observed when the proportion of steam is increased beyond 5.6 per cent may be due to a variety of causes; to the steam acting as a diluent; to an increase in the extent to which water is unburnt by the carbon monoxide; and, perhaps, in no slight measure, also to the tendency of the steam to hold back the oxygen.

6. It is to this last circumstance that the marked influence of oxygen in retarding combustion is probably attributable. This influence is especially noteworthy in the case of electrolytic gas, inasmuch as excess of hydrogen has precisely the opposite effect, and nitrogen regards the explosion less than does an excess of oxygen. According to Dixon, the rates in metres per second, at which various mixtures of hydrogen and oxygen and of electrolytic gas and nitrogen explode, are as follows:—

4H ₂ : 4O ₂	3532		
3H ₂ : 4O ₂	3527		
2H ₂ : 4O ₂	3268		
H ₂ : 4O ₂	2821		
H ₂ : O ₂	2328	H ₂ : 1O ₂ + 1N ₂	2426
H ₂ : 2O ₂	1927	H ₂ : 1O ₂ + 1½N ₂	2055
H ₂ : 3O ₂	1707	H ₂ : 1O ₂ + 2½N ₂	1822
H ₂ : 4O ₂	1281		

In seeking for an explanation of this remarkable, if not paradoxical, behaviour of hydrogen, it is necessary to remember that, whereas both oxygen and water molecules diminish in stability as the temperature rises, the stability of hydrogen peroxide must be at a maximum at a high temperature—since its formation from oxygen and water is an endothermic process. In fact, it is to be supposed that water is readily oxidised at temperatures such as

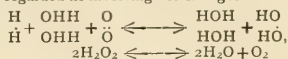
* The need of distinctive names for oxygen-stuff or atomic oxygen, and of the molecular oxygen we handle, is very obvious in discussing such a point.

† *Nernst, Zeit. Physik. Chem.*, 1903, vol. xlvii., p. 720, has endeavoured to deduce numerical estimates of the stability of hydrogen peroxide at high temperatures; the results arrived at, however, are not satisfactory owing to the paucity of data.

* A Paper Read before the Royal Society, June 16, 1904.

† W. A. Bone and R. V. Wheeler, "The Slow Oxidation of Methane at Low Temperatures," *Trans. Chem. Soc.*, 1902, vol. lxxxi., p. 536; 1903, vol. lxxxiii., p. 1074. W. A. Bone and W. E. Stockings, "The Slow Combustion of Ethane," *Ibid.*, 1904, vol. lxxxv., p. 693.

prevail in combustions. If, however, the formation of water be regarded as involving the changes—



it follows that water and oxygen will mutually hold each other in check; so that when electrolytic gas is exploded there will be a deficiency of oxygen, as it were, owing to its conversion into hydrogen peroxide, which may be regarded as relatively, if not entirely, inoperative as an oxidising agent at high temperatures in presence of oxygen. On the other hand, when excess of oxygen is present, the water—which is the effective catalyst—will be more or less held back, also in consequence of its oxidation to hydrogen peroxide. The marked influence of hydrogen in promoting the combustion of electrolytic gas is in full harmony with this conclusion; indeed, it is difficult to explain it in any other way than by supposing that, when present in excess, the hydrogen serves to promote the dissociation of the peroxide by diminishing the proportion of active oxygen present; in other words, according as hydrogen or oxygen is in excess, equilibrium is disturbed in one direction or the other. The interaction of hydrogen and oxygen may, perhaps, be supposed to be incomplete at high temperatures, less because the steam is partially dissociated than on account of the division of the oxygen between the hydrogen and water.

[Note added June 29.—The experiments on the oxidation of ethane at so low a temperature as 300, recently described by Bone and Stockings, have shown that change proceeds with surprising rapidity in the case of mixtures containing ethane and oxygen in the ratio 2:1 or 1:1, the oxygen disappearing within thirty to forty-five minutes, whereas when sufficient oxygen was present to burn the hydrocarbon completely to steam and carbon dioxide (1:2.5), a considerable quantity of oxygen and some ethane remained unchanged even after two days. There can be little doubt, therefore, that oxygen has a specific retarding effect even at so low a temperature as 300°, and there would seem to be no reason to suppose that the changes which occur at low temperatures are in any essential respect different from those at high temperatures].

AN ACCOUNT OF SOME PHENOMENA OBSERVED DURING THE ELECTROLYSIS OF CONCENTRATED SULPHURIC ACID.

By B. G. COBB.

THE description of the phenomena here considered is the result of the work of the writer during the past year.

In the first instance, the electrolysis of concentrated H_2SO_4 appeared to offer a very interesting subject for investigation.

In the earlier experiments electrodes of aluminium one-sixteenth inch in thickness were employed.

A current of E.M.F. 200 volts through an external resistance of 300 ohms was employed.

On switching on the current, the resistance of the acid was practically nil, but it soon rose, so that after half a minute only 0.02 ampère was passing.

The cause of this appears most probably to be the H_2 gas liberated from the - pole forming a non-conducting film.

The evolution of gas from the + pole was accompanied by very curious phenomena. Bubbles of gas appeared to dart all over the surface of the electrode.

On placing the apparatus in the dark the disengagement of gas was accompanied by very vigorous sparking beneath the liquid.

These sparks worked up and down the electrode with

regularity, until after ten minutes they occupied the whole surface.

An increase in the ampère caused the sparks to show greater activity.

After two hours thirty-five minutes resistance was such that E.M.F. was only 15 volts. The sparking was, however, quite as vigorous.

After protracted passage of the current the liquid became turbid with the separation of Al_2O_3 , $\text{Al}_2\text{O}_3 \cdot \text{Al}_2(\text{SO}_4)_3$, and free sulphur, caused presumably by the reduction of the acid.

Capillary action took place on the +, i.e., the sparking electrode, and it was observed that the sparks were quite as vigorous right outside the liquid, where the surface was wet, as underneath.

If the origin of the sparks was that the current was trying to pass from the anode through the liquid to the cathode, and (finding a non-conducting film of Al_2O_3) was temporarily interrupted, why should it prefer to spark above the liquid rather than to take the path of least resistance, i.e., straight down the electrode?

The + electrode before action weighed 4.40082 grms., and after fifteen hours 4.49901 grms.

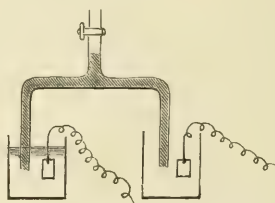
If a large current of 10 ampères be employed and the electrolyte kept cool, SO_3 is disengaged.

The current is, therefore, sufficiently powerful to overcome the great molecular attraction between SO_3 and H_2O . The presence of 0.05 per cent of water completely stopped sparking.

In using Pt electrodes no sparks are produced, but abundance of O_3 is liberated from the +, and a reddish-brown amorphous mass is formed on the - electrode.

Electrodes of pure electrolytic copper gave blood-red sparks after 2.5 hours.

(Syphon filled with acid.)



With a silver electrode for the + no sparks are noticed, but a black sticky mass (Ag_2O_2 , or $\text{Ag}_4\text{O}_?$) is produced.

Using Al electrodes and $\text{H}_2\text{S}_2\text{O}_7$, SO_3 is disengaged in the cold, but after fourteen minutes sparks cease entirely, thus differing from H_2SO_4 . Spectrum of sparks showed a line in the green of about 5200 wave-length. Voltage goes down for three hours, when it shows 6 volts, but later it rises to 16 volts, where it remains.

The addition of a small quantity of HNO_3 stops sparking temporarily, but it is soon resumed. On agitation of the liquid the sparks again cease. Ten days after an experiment, a beaker containing electrolysed acid, but from which the electrode had been removed, was found to evolve H_2S .

Al with Si dissolved showed no increase of sparking.

To some H_2SO_4 , $\text{K}_2\text{Mn}_2\text{O}_8$ was added, and the resulting Mn_2O_7 electrolysed. Sparking was then more vigorous, and after twelve hours liquid was colourless.

A solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 gave more vigorous sparks, and proved an excellent conductor.

After three hours sparks had ceased. They then reappeared, but on agitation ceased. (cf. HNO_3).

An experiment with the apparatus represented above showed, with a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 , a reduction to $\text{Cr}_2(\text{SO}_4)_3$ in the cell evolving O_2 .

An extraordinary effect is produced as follows:—

If a dry glass rod be caused to touch the top of the electrode + during electrolysis, an arc is produced under the liquid between the Al plate and the glass rod held in the hand.

In view of this the following experiment was devised:—

The - electrode was an Al plate and the + a stout Al wire wound round with glass-wool. On passing the current an arc starts between the + electrode and the glass-wool beneath the surface. A quantitative analysis of the aluminium used gave as a mean of six experiments:—

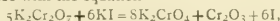
Aluminium	98.53451 per cent
Sulphur	1.44316 "
Insoluble residue	0.02233 "

June 26, 1904.

ON A NEW METHOD FOR THE PREPARATION OF PURE IODINE.*

By LANCELOT W. ANDREWS.

THE impurities to be looked for in iodine are moisture, hydriodic acid, bromine, chlorine, and cyanogen iodide. A number of processes have been suggested for obtaining a product free from these contaminations, among which may be mentioned the methods of Stas ("Nouvelles Recherches sur les Lois des Proportions Chimiques," p. 136), Wittstein (*Dingler's Poly. Journ.*, 1871, cc., 310), Mohr ("Titrimethode," 1874, p. 269), Meineke (*Chem. Zeit.*, 1892, xvi., 1219), and of Lean and Whatmough (*Journ. Chem. Soc.*, 1898, lxxiii., 148). All these methods are either very elaborate, demanding no inconsiderable sacrifice of time, or like the simple re-sublimation of iodine with potassium iodide, are inefficient. The reaction between fused potassium pyrochromate and potassium iodide, which occurs in accordance with the equation—



seemed to offer a possible and simple method for obtaining pure iodine directly from the impure iodide. A preliminary experiment showed that by fusing a mixture of 29.5 grms. of potassium pyrochromate with 20 grms. of potassium iodide, practically the whole of the iodine was obtained in the free state. No iodine was set free on fusing a mixture of normal potassium chromate and iodide. A mixture of potassium bromide (6 mols.) with pyrochromate (5 mols.) furnished, on fusion, a trace of free bromine, but when to the same mixture a little normal potassium chromate had been added, no bromine was set free. It should be said that all mixtures were made by rubbing the constituents thoroughly together in a mortar.

These experiments made it appear almost certain that if potassium iodide and pyrochromate were mixed together, with the former in moderate excess of the amount required by the equation, a product free from bromine and chlorine would be assured. Accordingly, 28 grms. of potassium pyrochromate were powdered with 20 grms. of potassium iodide and 1 gm. of potassium bromide, and the mixture was fused in a wide glass tube. Three and eight-tenths grms. of the sublimate were tested in the following manner for bromine:—The iodine was thrown into 100 c.c. of hot concentrated ammonia and a slight excess of silver carbonate was added, and the solution filtered. From the filtrate the silver was precipitated by hydrogen sulphide, and the liquid boiled down to a very small bulk with a little pure barium carbonate. The residue gave no reaction for bromine, either by the fluorescein test or on spectroscopic examination according to Lecoq de Boisbaudran (*Comptes Rendus*, 1881, xci., 902).†

To summarise, the following are the necessary steps in the preparation of pure iodine by the method given:—Pulverise potassium iodide with one and four-tenths times its weight of potassium pyrochromate, each salt having been previously separately fused to insure perfect dryness. Introduce the thoroughly incorporated mixture into a wide tube, closed at one end, and heat to about 200° in a current of dry air to expel any moisture which may have been taken up during the pulverisation. Place a plug of dry glass-wool over the mixture, and wipe out carefully the interior of the tube above the plug with absorbent cotton secured to a glass rod. Slip over the open end of the tube a second short one, fitting it as snugly as possible. Fix the tube at an angle with the horizontal, and heat the powder gradually with a small flame, using if necessary a screen of asbestos board. Having sublimed the iodine into the upper part of the tube, cut off the latter, when cold, at a point 2 or 3 c.m. above the glass-wool plug, or, if smaller amounts are being operated on, the tube can be melted off at the place indicated.

Chemical Laboratory, State Univ. of Iowa.

July 6, 1903.

Since sending the foregoing communication to the Editor of the *American Chemical Journal*, it has come to my knowledge through the last number of the *Centralblatt* (1903, i., 1435) that L. L. de Koninck has published in the *Bulletin de l'Académie Royale Belgique* (xvii., 15), a nearly identical method for the preparation of pure iodine. The priority, accordingly, belongs to him, but in view of the importance of the subject, it still appears worth while to publish the entirely independent confirmation of his results which my experiments afford; the more so since, so far as it is possible to judge from the abstract, his work does not directly demonstrate that the process can be so conducted as to insure the preparation of a product free from bromine.

July 25, 1903.

THE DETERMINATION OF FUSION POINTS.

By L. MAQUENNE.

THE fusing point of a substance, whether mineral or organic, is undoubtedly one of its most distinct characteristics, the same as its boiling point if it is volatile, or its rotatory point if it acts on polarised light.

All chemists are in agreement on this matter, and every one of us has had cause for regret on numerous occasions that the figures given by the earlier writers and reproduced in the older books are for the most part incorrect, sometimes by more than 100°, as in the case of leucine (E. Fischer, *Berichte*, vol. xxxiii., p. 2373).

Such errors are explained by the fact that they merely aim attached to fusion points the importance they merit; nothing, however, is more simple than to determine the fusing point of a pure substance with accuracy, when it is sufficiently stable not to undergo any decomposition at the temperature at which its change of state takes place. The choice of method and the manner of heating are therefore matters of indifference; the use of the capillary tube plunging into sulphuric acid is to be recommended, both on account of the rapidity of its indications and the simplicity of the materials necessary.

But the same is not the case when we have to deal with a substance easily decomposed; in this case the products of its decomposition mix with what remains intact of the material, and lower the fusion point by an amount which is greater as these products are more abundant. It is necessary therefore to operate as rapidly as possible.

With the object of obtaining a rapid heating we use the metallic block I described seventeen years ago, and on the subject of which in the short paper I wrote at that time, I saw no other advantage than that of doing away with the corrections necessary in the other methods (*Bull. Soc.*

* From the *American Chemical Journal*.

† Ascertained by acidifying a filtered sample with hydrochloric acid.

‡ This method rests on the observation of barium bromide lines at wave-lengths 535.8 and 520.6.

Chim., 1887, vol. xlviii., p. 771). In reality we only use it to observe instantaneous fusion points; that is to say, those effected in less than a second of heating, which cannot be done by any other arrangements.

Thus the block represents, not so much a particular apparatus as a veritable method of procedure, which, in the case of only slightly stable materials, appears to be to be infinitely superior to any other, inasmuch as it alone is capable of giving thoroughly concordant results.

This method appears still to be but slightly known, for in quite a recent paper A. Müther and M. Tollens compared the block with the capillary tube, saying that "mit dem bloc Maquenne soll man ähnlich verfahren" (with the Maquenne block we can proceed in a similar manner). We may enquire whether these authors found the same figures by both these methods, from which they conclude that the block offers no advantages (*Berichte*, vol. xxxvii., p. 313).

This is a perfectly just and logical conclusion if we use the block as an apparatus for heating slowly; it is not so, however, when used as we use it for the instantaneous determination of fusion points. I think it necessary, therefore, once for all, and in spite of all the instructions which may be given when buying one, to describe minutely the method of procedure to be followed in order to make proper use of it.

As soon as the temperature rises we throw small quantities (about a tenth of a milligram) of the body under examination on to the surface of the metal from time to time, only leaving them there for an instant until the point is reached when fusion takes place instantaneously. We then allow the temperature to fall, and we continue the same manoeuvre while this goes on.

Thus, in the case of stable bodies, after a few attempts we arrive at two points hardly differing by the fraction of a degree, at which the body fuses instantly or does not fuse at all; their mean represents the true fusing point, identical with that given by the capillary tube. In this manner pure mannite (regenerated from its hexacetine) fuses on the block in a quarter of a second at 167° , and resists indefinitely at a temperature of 166.5° ; benzoic acid fuses instantly at 121.5° and remains solid at 121° , &c. These are types of bodies having very definite fusing points.

For unstable bodies the instantaneous fusion point, determined as above, is not equal to that observed in a capillary tube; while the latter varies with the time of heating and goes lower as the time is less, the former remains fixed, and consequently appears to give a true physical constant better than the other.

Thus the block is the only apparatus which enables us to follow the progress of a decomposition at a given temperature, and at the expense of a few milligrams of material we are able to collect more observations in half-an-hour than could be effected by twenty capillary tubes.

E. Fischer has fixed three minutes as the time necessary for obtaining a fusion at 205° (uncorrected) of phenylglucosazone; this time, relatively short compared with the usual methods, corresponds to an extremely slow heating with the block, on which the fusion ought to take place in a second at most. This accounts for the differences observed by Müther and Tollens in the fusion points for this body given by different writers, G. Bertrand and others.

To give an idea of their extent I will mention a few observations made with absolutely pure phenylglucosazone, with the idea of examining the influence exercised by preliminary heating on the value of its fusion point. The temperature of the block was kept steady, and the time necessary for liquefaction noted in seconds:—

Time (secs.)	..	190	70	35	15	10	5	Instantaneous.
Temperature	..	209°	205°	210°	215°	220°	225°	230°

It is clear, from the above, that the point 205.206° , generally admitted for this substance, is by no means abso-

lute, and that it can only be looked upon as a constant if we operate always under the same conditions. This conforms absolutely with the ideas put forward by E. Fischer on this subject some long time since.

With regards to leucine (regenerated from its cupric compound) we see that it volatilises on the block, without fusing, at all temperatures below 340° ; thus it seems to be infusible at ordinary pressures, and will only melt in capillary tubes at the commencement of decomposition.

These remarks show that to define the fusion point of a substance that decomposes under the action of heat, it is indispensable to detail the circumstances under which the observation was made. This seems to us to be a habit as useful to acquire as to give the nature of the solvent, the concentration of the solution, and the temperature of the observation, when stating a rotatory power.

I may add, finally, that the determination of the instantaneous fusing point, whether obtained with the block or by any other means, no matter which, dispenses with these accessory facts, and consequently should be preferred to the ordinary so-called fusion points.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 8).

INTERNATIONAL TABLE OF ATOMIC WEIGHTS.

THE following letter has been addressed to the members of the Great International Committee on Atomic Weights:—

We feel called upon to submit the following matter to the judgment of the committee:—

As is well known, the committee was formed in order to introduce uniformity in two points: (1) the standard of atomic weights, (2) the atomic weights of the different elements.

In order to form a decision on the first point, *i.e.*, the question of whether $H=1$ or $O=16$ should be accepted as the standard, the matter was put to the vote (*Berichte*, 1900, xxxiii., II., 1878) in the year 1900, with the result that of the forty-nine members of the committee forty were in favour of $O=16$, only seven of $H=1$, and finally two were for the use of both standards. Thus it was determined by a large majority to introduce $O=16$ in future as the international basis of atomic weights.

With regard to the second point, the committee unanimously resolved to elect a special international committee to be entrusted with the yearly issue of a table of atomic weights corresponding to the latest point of view. The result of the votes (*Berichte*, 1902, xxxv., II., 4029) taken in the year 1902 was the election as members of Messrs. F. W. Clarke, Washington (President), T. E. Thorpe, London, K. Seubert, Hanover, who, we are pleased to say, were subsequently joined by M. H. Moissan, Paris (*Berichte*, 1904, xxxvii., I., 7). It is well known that this special committee has already begun its activity, and has established the atomic weights of all the elements for 1903 and 1904 with great circumspection. The committee, however, has thought fit to issue two tables of atomic weights on the basis of $O=16$ and of $H=1$.

This latter proceeding is, indeed, the cause of the present address. We have been petitioned from various quarters to protest against this, since it is clear that in this way the former abuse of two different tables of atomic weights being in use will be re-established, and the agreement on the subject of the atomic weights basis already arrived at, be brought to naught.

To begin with, we have received from the Council of the German Chemical Society the following resolution (*Berichte*, 1904, xxxvii., I., 5), passed in a sitting held on January 6th, 1904:—

"The Council deposes the Committee on Atomic Weights of the German Chemical Society to endeavour so to determine the International Committee on Atomic Weights that the continuation of two different tables of atomic weights,

based upon different units, may be put an end to as soon as possible."

Moreover, the President of the Imperial Board of Health in Berlin presented an address on this subject, dated February 23rd, 1904, to the Council of the German Chemical Society, and which was passed on by the latter to us (*Berichte*, 1904, xxxvii., 1., 999). The address reads as follows:—

"The efforts of the German Chemical Society to bring about a uniform basis for the calculation of atomic weights have lately led to the result that two tables have been suggested by the Special International Committee on Atomic Weights, consisting of Messrs. Clarke, Seubert, and Thorpe, for the year 1903 (*c.f. Berichte*, 1904, xxxvi., p. 5—10); one table calculates on the basis of oxygen = 16, the other on that of hydrogen = 1. The committee started from the consideration that the time was not yet come for a settled and formal decision on the fundamental question of the basis of atomic weights, and that it must be left to a future development to decide which of the two standards is the more suitable.

In the same way the committee for the year 1904, which has in the meantime been joined by M. Moissan, has again published two tables of atomic weights (*c.f. Berichte*, 1904, xxxvii., p. 7—10). This issue, although only a temporary one, by no means fulfils the expectations which induced the investigations of the unit of atomic weights, and which, above all, aimed at the agreement of a common obligatory unit for all chemists.

The problem seemed about to be solved when the Committee on Atomic Weights, chosen at the incitement of the Imperial Board of Health by the German Chemical Society on December 1st, 1897, to which Messrs. Landolt, Ostwald, and Seubert belonged, came to a decision in favour of the oxygen basis, and proposed a table of atomic weights, the calculations being based on the atomic weight of oxygen = 16, for general use (*c.f. Berichte*, 1898, xxxi., p. 2761—2768).

A table calculated on this basis has been subsequently re-published in the reports of the German Chemical Society in the first numbers of the annual reports for 1899 and 1900, and these figures for atomic weights thus appeared certain of general acceptance.

It must, however, be attributed to the subsequent opposition to these figures raised by a number of chemists (*c.f. among others Berichte*, 1900, xxxiii., p. 1847—1883; also 1901, xxxiv., p. 4353—4384; 1902, xxxv., p. 1240, 4028—4030; 1903, xxxvi., p. 3759—3766) that in the year 1901 the figures relating to hydrogen = 1 were also added to the table of atomic weights of the German Chemical Society, under the name of "didactic atomic weights." As has been already mentioned, the principal point of the matter was then left undecided by the special International Committee on Atomic Weights, and the solution of the problem put off to a later time (*c.f. Berichte*, 1903, xxxvi., p. 5—10).

I shall not here enter into the scientific arguments brought forward for and against the basis of oxygen = 16, but shall only briefly point out what confusions must follow if in future both tables are to remain in use, and that it is necessary for practical reasons to form a decision on the choice of the unit of atomic weights as speedily as possible.

Whereas a number of manuals of chemistry published within the last few years have accepted the oxygen basis of atomic weights, we find in others the atomic weights based upon hydrogen = 1. Thus even the students of chemistry are in danger of becoming accustomed to the use of different tables, by which the possibility of an agreement is even further deferred.

Should both tables remain in use in future, confusions and mistakes in analytic work will be unavoidable. With respect to this we need only point out that it may, under certain conditions, be impossible to learn the true contents of a solution, if this be only given, in the written passage in question, in gramme equivalents or in the form of

standard solutions, or that in comparing the results of different experiments a constant reduction will be necessary, if one experimenter has based his results on the unit of hydrogen, the other referring to the basis of oxygen. This would finally lead to the necessity of always ascertaining the concentrations of solutions and liquids for titration on the basis of both standards in order to avoid the difficulties mentioned. Yet this state of things must be designated as both unpractical and unscientific.

The view that the basis of oxygen is preferable to that of hydrogen appears to have spread latterly, to which fact the acceptance of this standard in a large number of manuals of chemistry bears witness. Moreover, I must add for the German Imperial Board of Health that in consequence of the resolutions of the German Committee on Atomic Weights for the year 1898, in the Pharmacopœia for the German Empire, fourth edition, 1900, which is still in force, the standard of oxygen = 16 is accepted, likewise that the "oxygen atomic weights" were recommended to the "Commission Deutscher Nahrungsmittelchemiker," the "Verein Deutscher Chemiker," and the "Verbande öffentlicher Chemiker" by the German Imperial Board of Health for their acceptance and sole use in the future. Thus the Board of Health is not in a position to give up the "oxygen atomic weights" without contradicting its former instructions, especially as in all probability the present regulations of the German Pharmacopœia will remain in force until 1910.

I therefore venture to recommend to the notice of the Council of the German Chemical Society that the German Chemical Society might perhaps succeed in a second attempt to establish uniformity among chemists with respect to the basis of atomic weights, and to bring the standard of oxygen = 16 into general use.

(Signed) KÖHLER.

In consideration of the above address we are now induced to obtain the opinion of the general committee on this subject, and to beg them to decide whether the following proposal shall be made to the special committee.

The Special Committee on Atomic Weights is requested for the future—

- (a) To issue only one table of atomic weights;
- (b) To choose the one based upon O = 16.

We venture to add the following remarks.

The proposal corresponds to the resolution of the general committee of the year 1900. The reasons which then determined the majority of the members to favour the oxygen basis will be found in their written answer (*Berichte*, 1900, xxxiii., II., p. 1851—1877) to our interrogation on March 30th, 1899. As we have frequently shown in former publications (*Berichte*, 1898, xxxi., III., 2761—2768; 1900, xxxiii., II., 1878—1881; xxxvi., III.), these are based chiefly upon the fact that, as is well known, the determination of atomic weights was always first attempted in relation to oxygen (Berzelius, Stas, Marignac), the figures relating to H = 1 being calculated from the former by means of the relationship, ascertained by experiment, of O : H. After the figures 15.96 : 1, which were formerly used, had been proved to be too high, the value of 15.879 ascertained by Morley was substituted, and this (15.88) was made use of by the International Committee on Atomic Weights in drawing up the table based upon H = 1.

The hope has been expressed that the figures ascertained with the greatest care by Morley will probably undergo no more changes in future, and therefore the reduction of atomic weights from the basis O = 16 to that of H = 1 be ensured. Nevertheless, we must conclude this question not to be entirely settled yet from the calculations (*Proc. Royal Society*, 1904, lxxiii., 153) published by Lord Rayleigh at the beginning of this year on the density of some gases at a low pressure. Whereas under the usual atmospheric pressure the relationship of the densities of O : H = 16 : 1.0076, it was found that in cases of extreme rarefaction, for which only Avogadro's law strictly holds good, the value of

16:10088 is assumed. If we take $H=1$ we therefore have the result $O=15.86$, and the atomic weights calculated on this basis will all be 0.13 per cent lower than those until now derived from $O=15.88$. Thus we shall find, for example, the following alterations:—

	$H=1.$		Diff.
	$O=15.88.$	$O=15.86.$	
Chlorine	35.18	35.14	0.04
Bromine	79.36	79.26	0.10
Silver	107.12	106.99	0.13
Iodine	125.90	125.74	0.16
Platinum	193.3	193.05	0.25
Uranium	236.7	236.4	0.3

The former uncertainty is therefore by no means removed, and the evil of atomic weights which have been established with the greatest care in relation to oxygen being deprived of their accuracy by the doubtful reduction to $H=1$ continues. If, however, we leave the former unaltered, the atomic weight of hydrogen alone is submitted to an entirely immaterial change (1.008 or 1.009), and the difficulty disappears entirely.

If some chemists, especially in Germany, still favour the former basis of $H=1$, this is due partly, as may be seen from various utterances (*Berichte*, 1900, xxxiii., II., 1853—1877; and 1903, xxxiv., III., 4354—4379), to the force of habit, partly to the fact that for the elementary teaching of chemistry it appears easier to start from the unit of hydrogen. This method is, however, also in future possible for those masters who prefer it, as in treating the theory of the derivation of atomic weights round numbers are always employed, and it is of no importance whether they refer to hydrogen or to oxygen. Later, when the methods of the exact estimation of atomic weights are entered into, it can be said that in order to establish greater accuracy the basis of oxygen with the value of $O=16$ is more reliable. A difficulty, from a didactic point of view, would not exist unless quite a different figure were to be chosen for oxygen.

Furthermore, we must oppose the view (*Berichte*, 1903, xxxvi., II., 4300), that especially the employment for some time past of the oxygen atomic weights for the calculation of the physical constants in which molecular weight is concerned, has determined physical chemists to strive for the general acceptance of the former. Had cogent reasons ever been brought forward to prove the greater trustworthiness of the hydrogen atomic weights, we should never have shrunk from reducing these constants to the other standard.

After the above discussions it is impossible to doubt that in the case of a choice between the oxygen and hydrogen tables, the preference must be accorded unconditionally to that of oxygen. This view has spread continually during later years. In most of the new chemical works (c.f. a list in the *Berichte*, 1903, xxxvi., III., 3764) belonging to various countries we find that the oxygen atomic weights have been adopted, and this is also the case in almost all the modern experimental work in inorganic and physical chemistry.

We have finally to discuss the question whether special reasons exist, making it appear desirable to publish the table based upon hydrogen as well as the one based upon oxygen, as the special committee has until now done. The latter have accounted for their mode of action in the following words (*Berichte*, 1903, xxxvi., I., 6):—

"It appears impracticable to form a definite and formal decision on the fundamental question of the basis of atomic weights. The Committee on Atomic Weights of the German Chemical Society had decided, it is true, in favour of the oxygen standard, but this proposal was met with both lively support and serious opposition. Indeed, on counting the votes it would seem that the opinions on this subject are pretty equally divided between 'pros' and 'cons,' and already polemic literature to an almost alarming extent has appeared on the question. Therefore it appears impossible

to accept one of the two standards, oxygen or hydrogen, and for the present both will still remain in use. Here experience must decide, finally the standard which most uniformly fulfils the demands of chemical and physical investigation will remain victorious, while the other will gradually fall into disuse."

In answer to this we may remark that not only did the Committee on Atomic Weights of the German Chemical Society accept the oxygen standard, but, as already mentioned, the Great International Committee also declared in favour of it, after putting it to the vote in 1900, by a large majority (forty votes for O, seven votes for H). If later (1901) a number of German chemists supported the hydrogen basis (*Berichte*, 1901, xxxiv., III., 4354—4379), thus changing the proportion to seventy-eight votes for O and hundred and six for H, this result was extremely defective, since the opinions of the chemists not included in the International Committee belonging to all the other countries were entirely wanting. No one can say what the result would have been had the other countries shown as lively an interest in the question as Germany. In consideration of this uncertain state of affairs, it is clear that the decision of the Great International Committee alone can come into question (we have already discussed this matter in the *Berichte*, 1903, xxxvi., III., 3766).

We quite share the opinion that it is impossible to force the acceptance of one of the two standards. But, on the other hand, the evil consequences resulting from the existence of two tables of atomic weight can be discussed. One of these is that all the molecular weights will differ, and consequently also the physical and chemical constants derived from them, which may lead to most prejudicial confusions. Secondly, the meaning of the standard solutions will be uncertain, and it will be necessary to add to the statement of every titre to which standard of atomic weights it refers. We shall have two systems of liquids for titration, which, if not carefully kept apart, but by mistake used together, would lead to the most incorrect results. As long as there are two tables included in manuals of chemistry, partly the one and partly the other will be adopted by the different chemists, and it is impossible to foresee an end to the confusion. The hope of one of the tables disappearing of its own accord can never be fulfilled, if the chemists are still presented with the publication of both tables by the International Committee.

Based upon the above arguments we finally repeat our former question, whether the members of the Great International Committee agree to a petition to the Special Committee in future only to issue one table of atomic weights, and to let it be the one based upon $O=16$. In order to save trouble in answering we enclose a formula, and beg it to be returned as soon as possible to Professor Landolt, 14, Albrechtstrasse, Berlin, N.W. 6.

Finally we have to announce the following changes in the membership of the Great International Committee. The place of the late Professor Dr. J. Wislicenus, of Leipzig, has been taken, at the proposal of the Kaiser Franz Joseph's Academy in Prague, by Professor Dr. B. Brauner of that town, to whom, as is well known, we owe the determination of the atomic weights of many rare kinds of earth. We venture to assume that the committee will approve this.

The Committee on Atomic Weights of the German Chemical Society:—

H. LANDOLT.
W. OSTWALD.
O. WALLACH.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst. The Duke of Northumberland, K.G., President, in the Chair. Viscountess Gort, Mr. M. H. Spielmann, and Mr. W. R. W. Sullivan were elected Members.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 15th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

(Concluded from p. 211.)

126. "Differentiation of Primary, Secondary, and Tertiary Amines." (A Preliminary Note.) By JOHN JOSEPH SUDBOROUGH and HAROLD HIBBERT.

L. Meunier (*Comptes Rendus*, 1903, cxxviii., 758) has shown that primary and secondary amines react with magnesium methyl iodide in ethereal solution according to the equations $RNH_2 + CH_3 \cdot MgI = RNH \cdot MgI + CH_4$ and $RR'NH + CH_3 \cdot MgI = RR'N \cdot MgI + CH_4$.

It is now shown that with primary amines and a solution of magnesium methyl iodide, in amyl ether the reaction proceeds quantitatively in the cold, as stated by Meunier, but that when the solution is heated a second molecule of methane is set free, presumably according to the equation $RNH \cdot MgI + CH_3 \cdot MgI = RN(MgI)_2 + CH_4$.

When a secondary amine is used, only one molecule of methane is evolved for each gram-molecule of the compound, even on heating.

Tertiary amines do not evolve any gas when mixed with Grignard's reagent.

The compounds examined so far have been *p*-toluidine, *β*-naphthylamine, diphenylamine, carbazole, and dimethylaniline. It is the intention of the authors to extend the work, and on these reactions to base methods for the characterisation of amino- and imino-groups and for the estimation of the amounts of primary, secondary, and tertiary amine in a mixture.

127. "Influence of Radium Radiations on Labile Stereoisomerides." By JOHN JOSEPH SUDBOROUGH.

The relative effects of exposing labile stereoisomerides to sunlight and to radium radiations have been examined. The substances used were *allo*-cinnamic, *α*-bromo-*allo*-cinnamic, and *β*-bromo-*allo*-cinnamic acids.

It has been already shown (*Trans.*, 1903, lxxxiii., 685, 1166) that these acids are transformed to a large extent into the more stable isomerides by the action of light or heat.

Prolonged exposure in the dark to the rays from pure radium bromide (1 mg.) does not affect the melting points of the acids.

The three acids, melting respectively at 68°, 120–121°, and 159–160°, were exposed to the radiations during a period of four months: at the end of this time no change in appearance and practically no alteration in melting point could be detected; the melting points found were 68°, 118–121°, and 158–160°. Specimens of the same acids were exposed to sunlight on March 17th, and by April 7th the melting points were considerably affected. The *allo*-cinnamic acid then began to melt at 60°, the *α*-bromo-*allo*-acid at 100°, and the *β*-bromo-*allo*-acid at 145°. On June 13th, the *allo*-cinnamic acid began to melt at 60° and was nearly completely fused by 120°, although a small amount of solid still remained at 145°. The *α*-bromo-*allo*-acid began to melt at 90° and was completely fused at 105°; the *β*-*allo*-acid began to melt at 120° and was completely fused at 135°, thus indicating that the three *allo*-acids are transformed into the stable isomerides more readily under the influence of light than by prolonged exposure to radium radiations.

128. "Notes on Analytical Chemistry." By GILBERT THOMAS MORGAN.

I. The Separation of Arsenic by Distillation in Hydrogen Chloride.—A modification of Piloty and Stock's apparatus (*Ber.*, 1897, xxx., 1649) was described, in which the mixed sulphides of arsenic and antimony were distilled in a current of hydrogen chloride, so that the vapours did not

come into contact with organic matter until after passing through a cooled aqueous solution of hydrogen sulphide.

In dealing with a mixture containing arsenic in the two states of oxidation, the distillation was first carried out in hydrogen chloride, when the arsenious sulphide precipitated in the receiver represented the tervalent arsenic. On repeating the distillation of the residual liquid in a current of hydrogen chloride mixed with hydrogen sulphide, a second precipitation of arsenious sulphide was obtained, this being derived from the arsenic originally present in the quinquivalent condition.

II. The Estimation of Carbon by Oxidation with Chromic Acid.—Phosphoric acid was substituted for sulphuric or hydrochloric acid in the gravimetric estimation of carbon dioxide in native carbonates, and when these substances contained organic matter, chromic acid was subsequently added to the contents of the distilling flask and the operation repeated, the second increase in weight of the tared absorption tube being due to the oxidation of the organic carbon.

The mixture of chromic and phosphoric acids was also used in estimating the total carbon in cast-iron and ferromanganese, the employment of a non-volatile acid instead of sulphuric acid obviating the risk of carrying over acid fumes into the weighed absorption tube.

129. "Nitrogen Chlorides containing Two Halogen Atoms attached to the Nitrogen." By FREDERICK DANIEL CHATTAWAY.

Very few substituted nitrogen chlorides containing two halogen atoms attached to a single nitrogen atom have been prepared, the best known being those derived from the primary alkylamines.

Stable, well-crystallised compounds having the general formula $RSO_2 \cdot NCl_2$ are yielded by all the sulphonamides, and a few have already been described by Kastle, Keiser, and Bradley (*Amer. Chem. Journ.*, 1896, xviii., 491).

They are most easily prepared by dissolving the sulphonamides in a solution of bleaching-powder and adding acetic acid, when they separate as crystalline solids.

The dichloroaminosulphonamides are not easily hydrolysed even by boiling with water; they dissolve in caustic alkalis, apparently yielding salts of the monochlorosulphonamides, which can be re-crystallised from water. With hydrochloric acid, hydriodic acid, or alcohol, they react vigorously, the sulphonamides are regenerated, and chlorine, iodine, or ethyl hypochlorite is liberated. On heating rapidly, the dichlorosulphonamides decompose with slight explosion, whilst the tetrachlorodisulphonamides explode with great violence. This behaviour is noteworthy, as the latter compounds are the only substituted nitrogen chlorides yet prepared which detonate in a way resembling the explosion of nitrogen chloride itself.

These compounds, as well as the chlorosulphonalkylamides and the corresponding bromine derivatives, are being further studied, as they are very reactive and promise to be of considerable value in organic synthesis. Moreover, the dichlorosulphonamides are so easily prepared, crystallised, and analysed that they may prove of considerable use in the investigation of sulphonic acids.

The following compounds were described:—

Benzenesulphondichloroamide, $C_6H_5 \cdot SO_2 \cdot NCl_2$, colourless plates, m. p. 76°; *p*-toluenesulphondichloroamide, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl_2$, long, four-sided prisms, m. p. 83° (Kastle, Keiser, and Bradley, *loc. cit.*); *o*-toluenesulphondichloroamide, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl_2$, colourless plates, m. p. 33°; *m*-nitrobenzenesulphondichlorodiamide, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot NCl_2$, faintly yellow, six-sided plates, m. p. 121°; *o*-nitrobenzene-*p*-sulphondichloroamide, $CH_3 \cdot C_6H_4 \cdot (NO_2) \cdot SO_2 \cdot NCl_2$ (1:2:4), pale yellow, four-sided prisms, m. p. 101°; benzene-*m* disulphontetrachloroamide, $C_6H_6 \cdot (SO_2 \cdot NCl_2)_2$, colourless rhombs, m. p. 128°; naphthalene-1-sulphondichloroamide, $C_{10}H_7 \cdot SO_2 \cdot NCl_2$, pale yellow plates, m. p. 91°; naphthalene-2-sulphondichloroamide, colourless plates, m. p. 68°; naphthalene-2:7-disulphontetrachloroamide, $C_{10}H_6 \cdot (SO_2 \cdot NCl_2)_2$, clusters of colourless pyramids, m. p. 165°; anthraquinone-

2-sulphondichloroamide, $C_{14}H_7O_2 \cdot SO_2 \cdot NCl_2$, yellow plates, m. p. 177°.

130. "Sulphonphenylchloroamides and Sulphontylchloroamides." By FREDERICK DANIEL CHATTAWAY.

In a paper on the action of sodium hypochlorite on the aromatic sulphonamides, Raper, Thomson, and Cohen (*Trans.*, 1904, lxxv., 371) state that they were unable to obtain benzenesulphonphenylchloroamide, which was too unstable to be isolated in a pure state. This and other similar compounds can, however, easily be obtained if precautions are taken to avoid the presence of catalytic agents which bring about transformation. They are well-crystallised, comparatively stable substances, and show the characteristic behaviour of chloroamino-derivatives. The method of preparation and the properties of benzenesulphonphenylchloroamide and of a number of similar compounds were described.

131. "Stereoisomeric Glucoses and the Hydrolysis of Glucosidic Acetates." By EDWARD FRANKLAND ARMSTRONG and PAUL SEIDELIN ARUP.

The results obtained on hydrolysing several of the glucosidic acetates by alkali were described and discussed in the light of the evidence recently brought forward regarding the stereoisomeric glucoses. It was shown that the acetyl groups are removed with unequal readiness from the penta-acetates of glucose and galactose and from sucrose octoacetate, and with equal readiness from the tetra-acetates of the methylglucosides and galactosides. Kreman's observation (*Monatsh.*, 1902, xxiii., 479) that the two isomeric penta-acetates of glucose are hydrolysed at equal rates is confirmed.

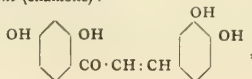
132. "The Colouring Matter of the Flowers of *Butea frondosa*." By ARTHUR GEORGE PERKIN.

In a former communication (J. J. Hummel and A. G. Perkin, *Proc.*, 1903, xix., 134), it was considered probable that butein from *Butea frondosa* exists in a colourless as well as in a yellow form. These modifications are, however, distinct substances. The colourless compound now termed *butin*, $C_{15}H_{12}O_5$, crystallising from alcohol in colourless needles and from dilute alcohol in pale yellow needles with H_2O , melts at 224–226°. The *triacetyl* compound, $C_{15}H_9O_5(C_2H_3O)_3$, forms colourless leaflets (m. p. 123–125°), and the *bensoyl* compound, $C_{15}H_9O_5(C_6H_5O)_3$, colourless needles (m. p. 155–157°). On fusion with caustic alkali, butin gives resorcinol and protocatechuic acid, and at a lower temperature resacetophenone is also formed. By methylation, two isomeric methyl ethers, $C_{15}H_{13}O_5$, are produced: (a) yellow leaflets (m. p. 156–158°) containing a free hydroxyl group, and (b) almost colourless, flat needles (m. p. 119–121°).

Butein, $C_{15}H_{12}O_5$, orange-yellow needles (m. p. 213–215°), crystallises from dilute alcohol with H_2O ; it is obtained in small quantity together with butin from the plant, and can be prepared from butin by the action of hot dilute caustic alkali or alcoholic potassium acetate; *acetylbutein*, $C_{17}H_{15}O_5(C_2H_3O)_2$, forms pale yellow needles (m. p. 129–131°). On fusion with alkali, butein gives the same decomposition products as butin, and on methylation the same two trimethyl ethers, (a) m. p. 156–158°, and (b) m. p. 119–121°.

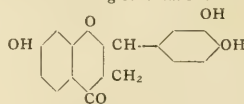
When digested with boiling dilute alcoholic sulphuric acid, butein is partially reconverted into butin, and by digesting the trimethyl compound (m. p. 119–121°), which is really butin methyl ether, with alcoholic potash and water, it passes into the butein methyl ether (a) (m. p. 156–158°). Again, on digesting butein methyl ether with alcoholic sulphuric acid butin methyl ether is obtained.

Butein has the constitution of a tetrahydroxybenzylideneacetophenone (chalcone):—

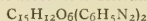


as proved by the synthesis of its trimethyl ether (m. p. 156–158°) by the condensation of veratric aldehyde with resacetophenone monomethyl ether.

Kostanecki and his colleagues (*Ber.*, 1904, xxvii., 784) have shown that with dilute sulphuric acid chalcone methyl ethers give the corresponding flavanone compounds, and as both butein and its methyl ether in this way yield butin and its methyl ether respectively, there can be little doubt that butin has the following constitution:—



133. "Cyanomaclurin." By ARTHUR GEORGE PERKIN. Cyanomaclurin (*Trans.*, 1895, lxvii., 937) which exists in jackwood (*Artocarpus integrifolia*) in conjunction with morin, crystallises from water in the anhydrous form, and is now shown to be isomeric with the catechins, $C_{15}H_{14}O_6$; it forms a *penta-acetyl* compound, $C_{15}H_9O_6(C_2H_3O)_5$, separating in colourless needles (m. p. 136–138°, a *pentabenzoyl* compound forming colourless prisms (m. p. 171–173°), and the azobenzene derivative—



(m. p. 245–247°), gives an *acetyl* compound melting at 209–210°. On fusion with caustic alkali, cyanomaclurin gives β -resorcylic acid (not cresorcylic acid as previously suggested) and phloroglucinol, and with pine wood and hydrochloric acid it resembles the catechins in giving the phloroglucinol reaction. With boiling dilute hydrochloric acid, a brown amorphous compound is produced; this is identical in appearance with the so-called fourth anhydride from Gambier catechin, and has the same percentage composition.

Cyanomaclurin thus appears to represent a catechin in which the catechol nucleus is replaced by resorcinol.

134. "The Determination of Acetyl Groups." By ARTHUR GEORGE PERKIN.

The substance (approximately 0.5 gm.) in 30 c.c. alcohol is distilled with 2 c.c. of sulphuric acid, a little fresh alcohol being added from time to time. The distillate is collected in standard alcoholic potash, and this is boiled in order to saponify the ethyl acetate present, the mixture being subsequently titrated with sulphuric acid. The operation is complete in about an hour and sufficiently accurate for general use. The following results have been obtained:—

	Gave acetic acid.	Theory.
Acetylalzarin	= 37.59	37.04
Acetylquercetin	= 58.44	58.59
Acetylpuropurgallin	= 62.40	61.86
Acetylcatechin (m. p. 129–130°)	= 60.18	60.00
Acetylcatechin (m. p. 158–160°)	= 60.24	60.00
Acetylbutin	= 45.60, 45.34	45.23

With acetanilide and its homologues reliable results are also obtained, employing, however, 4 c.c. of sulphuric acid, and longer distillation. Thus acetanilide itself gave acetic acid = 44.74 and 44.55 per cent, whereas theory requires 44.44. It has been previously shown that, with alcoholic potassium acetate, acetyl derivatives of the phenols evolve ethyl acetate. This process can be employed for acetyl determinations in some instances, and is still under investigation, but as yet has not been successful in all cases. By this means acetylbutin gave 45.60 (*ante*) and acetylbutin 54 per cent; in the latter case the theory requires 54.54 per cent.

135. "Note on the Catechins." By ARTHUR GEORGE PERKIN.

In a previous communication (*Trans.*, 1902, lxxxi., 1760) it was pointed out that whereas Gambier catechu contains a catechin, $C_{15}H_{14}O_6$ (m. p. 175–177°), the pentabenzoyl derivative of which melts at 151–153°, yet a

catechin, $C_{15}H_{10}O_6$, which was isolated from *Acacia catechu*, melted at $204-205^\circ$, and gave a benzoyl compound, melting at $181-183^\circ$. It is now found that the acacia catechin gives an acetyl derivative, $C_{15}H_9O_6(C_2H_3O)_2$, forming colourless needles (m. p. $158-160^\circ$), and a tetramethyl ether, $C_{15}H_{10}O_2(OCH_3)_4$, separating in colourless prisms (m. p. $152-153^\circ$). The corresponding substances from the Gambier catechin (Kostanecki and Tambor, *Ber.*, 1902, xxxv., 1867), melt at $129-130^\circ$ and at $142-143^\circ$ respectively. For acacia catechin the name "*acacatechin*" is proposed.

136. "*A Constituent of Java Indigo.*" By ARTHUR GEORGE PERKIN.

Rawson (*J. Soc. Dyers and Colourists*, 1899, xv., 129) has shown that Java indigo contains a yellow colouring matter. This substance, $C_{15}H_{10}O_6$, forms yellow needles, melts at $276-277^\circ$, and gives an acetyl compound, $C_{15}H_9O_6(C_2H_3O)_2$, which separates in colourless needles and melts, when crystallised from methyl alcohol, first at $116-120^\circ$ and subsequently at $181-182^\circ$. The colouring matter is identical with kampherol (*Trans.*, 1902, lxxxi., 587).

ROYAL DUBLIN SOCIETY.

At the final Scientific Meeting of this session, Prof. TICHBORNE read a paper "*On a General Method in Qualitative Analysis for determining the presence of an Oxide.*"

The determination of an oxide, the author said, in a mixture or by itself, was not always easy. It was, in fact, largely indicated by the negation of special reactions and by the analyst's knowledge of the special properties of the most well-known oxides.

The method proposed by the author is based upon the reaction of phenol-phthalein with acid carbonates and carbonates of the alkalis and the fact that most metallic oxides will reduce a certain proportion of the acid carbonate to the normal carbonate.

The test solutions used are—

(1) Phenolphthalein Solution.

(2) A 5 per Cent Solution of Pure Sodium Acid-carbonate in Distilled Water.—If this solution is tested with the phenol-phthalein it will probably give a faint pinkish colouration, although the carbonate may be perfectly pure. The act of dissolving it produces a slight dissociation. A few drops of normal acid are added until the solution is quite colourless when treated with phenol-phthalein. If this test solution has been laid by for some time it must be again brought to the neutral stage.

The insoluble suspected oxide may be rubbed in a mortar with the sodium acid carbonate solution and filtered, or it may be allowed to remain in contact with the solution for about two hours, occasionally shaking, and filtered. The filtrate in each case will strike a deep crimson colour with the phenol-phthalein if an oxide is present.

Almost all hydrated oxides and oxides made in the moist way decompose the sodium acid carbonate solution.

Mineral oxides, or oxides which have been ignited, with a few exceptions, behave badly in this respect.

Ferric oxide and alumina do not act, as the carbonates do not exist.

The following oxides will reduce the acid carbonate to the neutral salt of soda:—Oxides of lead, silver, bismuth, zinc (ignited and precipitated), copper, antimony, cerium, iron (other than Fe_2O_3), mercury, tin. Alumina and ferric oxide do not act.

Dr. WALTER ADENEY then made a verbal communication on the Aeration of Sea-water. A very long discussion followed which practically filled up the evening. No written paper was put in in connection with this communication.

Mr. Richard Moss was put down for what promised to be an interesting paper, but it was crushed out by the

above discussion and a communication on the "Mechanical Analysis of Soils." The title of Mr. Moss's paper was "On the State in which Helium exists in Pitch-blende."

NOTICES OF BOOKS.

The Metallurgy of Steel. By F. W. HARBORD, A.R.S.M., F.I.C. With a Section on the Mechanical Treatment of Steel, by J. W. HALL, A.M.I.C.E. With 37 Folding Plates, comprising 178 Figures, over 280 Illustrations in the text, and nearly 100 Micro-photographs of Steel Sections. The Metallurgical Series. Edited by Prof. Sir W. ROBERTS-AUSTEN, K.C.B., F.R.S. London: Charles Griffin and Co., Ltd. 1904. Pp. 758.

THE author of this ponderous volume set out with very ambitious intentions, viz., to produce a work comprising within the limits of one volume a full description of the various branches of Steel Manufacture, both from a metallurgical and an engineering standpoint, as well as to discuss the Physics and Chemistry of Steel in relation to its manufacture. The task he set himself was a heavy one, but on looking through the pages of this book we feel bound to admit that he has succeeded in achieving his object, and has given us a work that appeals alike to the Student, the Engineer, the Works Manager, and the Chemist.

The book is divided into four Sections:—(1) The Manufacture of Steel; (2) Reheating; (3) The Mechanical Treatment of Steel; and (4) Finished Steel.

The first Section, divided into twelve chapters, describes the manufacture of steel by the various known processes, not only from the practical, but also from the chemical or theoretical point of view. These processes comprise those involving the use of Bessemer converters, the Siemens open hearth, &c., and include the production of shear and crucible steels and armour plates.

Section 2, on "Reheating," is by Mr. Harbord, in conjunction with Mr. J. W. Hall, and consists of two chapters only, the first describing various reheating furnaces, and the second methods of handling material at and in these furnaces. We now come to Section 3, on the Mechanical Treatment of Steel, by Mr. J. W. Hall; this is a most important section and comprises twenty chapters, filling some 250 pages. The first matters dealt with are those connected with rolling and rolling mills; the various kinds of mills are described, and their adaptability to special kinds of work dwelt upon; while forging, compressing, tube making, and wire-drawing are each dealt with in separate chapters.

Section 4, on Finished Steel, is devoted principally to the testing of the finished article and the physical properties of finished steel. Some of the leading testing machines are described, and the influence of impurities on the mechanical properties of steel is discussed.

There is a valuable chapter on the heat treatment of steel, which has been attracting so much attention lately, especially in connection with high speed tool steels, and the methods of using, and the details of the latest forms of pyrometers are described. The microscopical examination of steel sections has also received adequate attention, and there are a number of excellent micro-photographs belonging to this branch of the subject. The index is a full one and adds to the value of this work as a book of reference.

The Elements of Chemistry. By M. M. PATTISON MUIR, M.A. London: J. and A. Churchill. 1904.

THE author of this most admirable and original text-book need have no fear that he has produced "one more illustrated catalogue of chemical odds and ends," which is

a very true description of the only class of book which was available for the use of the student of chemistry until quite recently; the marvel was under the old system that even the most promising learner ever had the perseverance to arrange and sort out the enormous mass of facts more or less baldly stated which was put before him, and to arrive at even the most primitive ideas concerning the fundamentals of the science. This state of affairs is now altogether changed, and this type of book illustrates excellently the methods which the best and most successful teachers have now adopted. The author gives us a scholarly and readable account of the principles of the science put forward in logical order and in a most characteristic manner. The facts he enumerates are quite sufficient for his purpose, and if a student works through the book, making himself practically acquainted with the more familiar compounds in the laboratory and consulting a chemical encyclopædia for the information concerning them which he cannot acquire experimentally for himself, he ought to obtain a first-rate knowledge of the subject, and to gain a very interesting insight into the philosophy of the science. One striking feature of this work, which can hardly be too highly spoken of, is the way in which the development of the science from the earliest times is put before the student in the most interesting historical notes and extracts; the author fully realises that the careful study of the steps in the development of a theory adds vastly to the ease with which a thorough understanding of that theory is acquired.

On reading down the titles of the chapters a doubt as to the convenience of the order in which the elements are taken up is bound to pass through the mind. The first elements studied in detail are very appropriately oxygen and hydrogen, then nitrogen, sulphur, potassium, sodium, and iron. Then arsenic, antimony, bismuth, tin, and the halogens are introduced, and phosphorus after a good many chapters on essentially theoretical branches of the subject. Carbon and silicon and the rest of the metals conclude the book, and the teacher would find it very difficult to alter the order successfully.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). V. Band. 9 Hft. Braunschweig: Friedrich Vieweg und Sohn. 1904.

THE June number of these *Beiträge* contains seven articles dealing almost entirely with physiological questions of only slight chemical interest. Siegfried Rosenberg and Carl Oppenheimer have examined the resistance of genuine albumen to tryptic digestion in the animal organism, and their numerous careful experiments, which are described in detail here, go to show that such resistance does occur within the organism as well as extra corpus. C. H. Rothera writes an account of his researches on the mode of combination in which nitrogen occurs in albumen. He finds that of the total nitrogen in chitin, for instance, about 88 per cent is present as monomino and amido nitrogen, the remainder being diamino and melanine, and he has also examined the ichthyne from the eggs of *Torpedo marmorata* with the object of deciding the same question relating to its nitrogen.

Jahrbuch der Radioaktivität und Elektronik. ("Journal of Radio-activity and Electronics"). Edited by JOHANNES STARK. Leipzig: S. Hirzel. 1904.

THE time has certainly come when radio-activity is to be regarded as an independent science, which deserves a periodical of its own, and from the distinguished names upon the title-page of this Jahrbuch, which is issued with the special co-operation of Prof. H. Becquerel and Sir William Ramsay, we may safely predict that it will be a worthy predecessor of others which will, no doubt, appear in other languages. The periodical is to contain chiefly extracts which will aid in the difficult task of keeping pace

with the enormous amount of literature dealing with radio-activity which is now appearing, but room will also be found for some original reports. This first number contains an article by Stark on the "Law and Constants of Radio-activity Changes," and a translation into German of R. J. Strutt's "Study of the Radio-activity of Certain Minerals and Mineral Waters," from the *Proceedings of the Royal Society*. Also it contains numerous abstracts of the papers which have appeared on various branches of the subject, so that if, for example, an investigator wishes to know something of the present state of our knowledge as regards the spectrum of radium, reference to the article by Precht on this point will not only give him a short account of the outlines of what he wants to know, but also a complete list of the papers dealing with it which have appeared. In the bibliography at the end of the journal an additional alphabetical list of the authors' names would be a great convenience.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 24, June 13, 1904.

Atomic Weight of Nitrogen. Analysis by Weight of Nitrogen Protioxide.—Ph. A. Guye and St. Bogdan.—The authors make a series of new determinations of the atomic weight of nitrogen, which are absolutely independent of the atomic weights of the elements Cl, K, Na, Li, and C, as they believe that the errors in the values of these latter are all accumulated in the atomic weight of the nitrogen. The experiment consists in finding the atomic weight of nitrogen relative to oxygen by an analysis of nitrogen protioxide without assuming any other atomic weights. As a mean of the numbers found, the value 14.007 may be considered as definite. The value found by physico-chemical methods being 14.002, it may be assumed that the actual value is at least below 14.01.

Decomposition of a Mixture of Calcium Carbonate and an Alkaline Carbonate under the Action of Heat in a Vacuum.—P. Lebeau.—The decomposition of mixtures of calcium carbonate with carbonates of caesium, rubidium, potassium, and sodium can be completely effected under the action of heat in a vacuum at a temperature near 1000°. This decomposition is more easily produced in the mixture than in calcium carbonate alone, and from the beginning of the dissociation the tension is decidedly inferior to that of this compound alone for the same temperature. This fact is in accordance with the existence of double carbonates of calcium and the alkaline metal possessing different dissociation temperatures.

Cuprous Salts.—A. Joannis.—The author proved in a former research that certain cuprous salts can be combined with carbonic oxide or with ammonia, and he prepared the sulphate $\text{SO}_4\text{Cu}_2 \cdot 2\text{CO} \cdot \text{H}_2\text{O}$. Since then he obtains analogous compounds by a new method, in which liquids which are very unstable in air can be evaporated in an atmosphere of carbonic oxide. The method consists in dissolving an ammonium salt in liquefied ammonia gas and allowing this solution to act on the red sub-oxide of copper. The following reaction takes place:— $2(\text{A} \cdot \text{NH}_4) + \text{Cu}_2\text{O} = \text{A}_2\text{Cu}_2 + 2\text{NH}_3 + \text{H}_2\text{O}$; A denoting a radical. The water and ammonia thus set free can combine or not with the salt formed. He applies this method to various mineral and organic salts, and by a slight modification applies it also to ammoniacal salts which are insoluble in liquefied ammonia.

A Basic Ferric Phosphate.—E. Berger.—Freshly precipitated hydrated sesquioxide of iron dissolves in an

excess of phosphorous acid. This solution is completely precipitated by water in excess, giving a white precipitate. This precipitate when not thoroughly washed has a variable composition intermediate between that of an acid and neutral phosphate. When, however, the precipitate is washed with cold water for several hours until the water is perfectly neutral, and the residue then dried first on a porous tile, then for several days *in vacuo* over sulphuric acid, a white powder of absolutely definite composition is produced. This is a basic ferric phosphate, and has probably the composition $(\text{PO}_3\text{H})_6\text{Fe}_4\cdot\text{Fe}(\text{OH})_3\cdot 5\text{H}_2\text{O}$.

Alloys of Aluminium with Bismuth and Magnesium.—Hector Pecheux.—The author succeeds in uniting the two metals bismuth and aluminium by melting them in a crucible in which the aluminium (melting at 550°) is first thrown, and then the bismuth (melting at 260°). Four homogeneous alloys are formed containing 75, 85, 88, and 94 per cent of aluminium. He also finds that aluminium and magnesium can be made to unite by maintaining the magnesium (melting at 450°) in the middle of the aluminium. Five definite alloys are thus obtained containing 66, 68, 73, 77, and 85 per cent of aluminium.

Iodine Compounds obtained with Metanitriline.—P. Brenans.—The author prepares iodine-nitrilines, and establishes their constitution by transforming them into iodo-nitrobenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot 1\cdot 1\cdot 4$. He compares this compound with its isomer, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot 1\cdot 1\cdot 4$, which is prepared by substituting the iodine of the NH_2 group in paranitriline, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot 1\cdot 4$, and establishes the fact that the two bodies from these two origins are absolutely identical.

A Product of the Spontaneous Alteration of Oxalacetic Ether.—L. J. Simon.—Oxalacetic ether, $\text{CO}_2\text{C}_2\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{C}_2\text{H}_5$, when kept for some time, undergoes a spontaneous alteration which shows itself by the violet colour which it takes in contact with alkaline reagents. This alteration can be adapted to a method of identification of the ether. It is really due to the formation of a dioxiquinonic derivative.

Rosaniline Polyacids.—Jules Schmidlin.—The author's researches are to discover which are the polyacids of rosaniline. The chlorhydrates which he obtains are very stable, and their preparation is based on the fact that the brown bodies described by Hofmann retain the acid in a state of solution. It is necessary to put these bodies in a vacuum for a month in presence of potash in order to completely remove the excess of acid. The brown crystalline mass then becomes completely black and odourless.

Bulletin de la Société Chimique de Paris.
Series 3, vol. xxix., No. 22.

Analysis of Commercial Nickel.—A. Hollard.—Already inserted in full.

The Composition of Gelatin rendered Insoluble by the Salts of Sesquioxide of Chromium, and the Theory of the Action of Light on Gelatin treated with Metallic Chromates.—A. L. Lumière and A. Seyewetz.—At the close of a long paper the authors arrive at several conclusions:—1. In the treatment with salts of chromium, the gelatin seems to fix the chromium directly, since its properties undergo profound modifications, and the chromium cannot be removed by numerous washings with boiling water. 2. The acid salt of chromium, although retained strongly by the gelatin, does not seem to have anything to do with the phenomenon of insolubilisation, since it can be removed without modifying the properties of the insolubilised gelatin. 3. A determined weight of gelatin fixes a constant maximum quantity of sesquioxide of chromium comprised between $3\cdot 2$ grms. and $3\cdot 5$ grms. per 100 grms. of gelatin, no matter what chromic salt be used for the insolubilisation; this seems to show that we

have to do with a perfectly definite compound. 4. On account of its easy dissociability, insolubilised gelatin is rather a compound of addition than a true combination. 5. The dissociation of chromised gelatin by repeated treatments with boiling water can be prevented, either by washing the gelatin treated with the chromium compound in ammoniacal water under suitable conditions, or by adding to the gelatin, before the addition of the chromium salt, the theoretical amount of ammonia to saturate the acid in this salt.

No. 23.

On the Hausmannites from Sweden.—A. Gorgeu.—Already inserted in full.

A Series of Artificial Quadratic Spinel of the Hausmannite Type.—A. Gorgeu.—The object of this paper was to make known a series of anhydrous saline oxides, of which pure hausmannite is the type, and which are crystallised in the same form in octahedra on a square base. The author has already thrown doubts on the existence of the sesquioxide of manganese as an acid element in the superoxides, because they are decomposed by nitric acid into the protoxide and the insoluble binioxide. However, he has repeated his experiments on the natural and artificial superoxides of manganese, but he used acetic acid diluted with from 3 to 10 volumes of water. Under these new conditions the composition of acerdes was not changed, and the same was the case when he submitted to the same treatment the anhydrous sesquioxides resulting from the prolonged calcination of acerdes or pyrolusite at a dull red heat. Treated in the same manner, hausmannite only gave up a third of its manganese in the form of manganous acetate, the insoluble portion containing the other two-thirds in the form of M_2O_3 . The author goes on to deal with the artificial hausmannites in which a portion of the manganese, viz., the manganous oxide, is replaced by another metallic oxide. He has succeeded in producing them in the case of zinc, magnesium, and cadmium, and gives analyses of these bodies. The examination of these results shows clearly that there is really a partial substitution, and that in the two latter cases especially, they represent the sesquimanganites of the form $\text{Mn}_2\text{O}_3\text{RO}$.

The Volcanic Ash from Mont Pelée, Martinique.—A. B. Griffiths.—Already inserted.

Derivatives of Lauric Acid.—G. Guérin.—The substance chosen by the author for the preparation of his lauric acid was a product obtained during the purification of oil of coco to extract the butter. It was first saponified and then treated with an excess of hydrochloric acid, and heated; the fatty acids were decanted, dissolved in ether, and distilled; the residue was then digested with an equal weight of pure methylic alcohol, and half that quantity of sulphuric acid for six hours to produce etherification. The cooled product was poured into a large quantity of water, the upper portion decanted and washed with 10 per cent carbonate of soda and distilled water, then dried completely. These methylic ethers were then distilled fractionally, and the products collected at every 5° . The first portions came over at 95° , the last at 275° . The lower fractions appeared to contain small quantities of capric acid, then he found caprylic acid, and the higher fractions corresponded to myristic, palmitic, and stearic acids. As for the fraction corresponding to lauric acid, it represented about 65 per cent of the ethers. The author then describes in detail the isolation of the caprylic acid, the preparation of lauric acid, lauro-orthotoluide, lauro-paratoluide, lauro-phenylhydrazide, chloride of lauryl, and bromolauric acid.

α -Hydroxylauric Acid, $\text{C}_9\text{H}_{19}\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{COOH}$.—G. Guérin.—This acid is prepared by placing 200 grms. of bromolauric acid in a porcelain crucible with 125 grms. of potassic hydrate and about 2 litres of water. Boil for two or three hours, keeping the volume constant; then cool. The alkaline solution of hydroxylaurate is then decomposed with hydrochloric acid in excess, and taken

up with ether; this latter is washed, decanted, and evaporated. The residue, dried at 100° *in vacuo*, is redissolved in chloroform, from which it is crystallised by cooling in ice. The crystals of hydroxylauric acid fuse at $73-74^{\circ}$. The author describes the preparation of several salts of this acid, such as the hydroxylaurate of sodium, potassium, copper, and lead, as well as its ethers and amides.

Undecylmethylketone.—G. Guérin.—This substance is prepared by reacting with 14.25 grms. of sodium wire on 80 grms. of acetylacetate of ethyl, previously diluted with 250 grms. of anhydrous ether; the reaction is a very lively one, and the flask must be kept cool. After about twenty-four hours, all the sodium has disappeared forming, acetylacetate of ethyl-soda, which is precipitated as a white mass. At this moment 100 grms. of chloride of lauryl are run in, and the whole is heated on the water-bath. After eight hours, cool, and treat the mass with a large excess of water. Add ether, wash and separate the ethereal layer, which is dried and distilled. The residue consists of a mixture of the O-ether and the C-ether, and weighs 140 grms., a return of 98 per cent. This product was saponified directly; the methylundecylketone formed, purified by crystallisation in methylic alcohol, fuses at 28° , and boils at $140-142^{\circ}$ under 14-15 m.m.

Transformation of Benzophenone into Triphenylcarbinol.—R. Delange.—If 100 grms. of benzophenone are mixed with the same weight of finely-powdered, dry potash, and heated to 170° for about twenty hours, about 15 or 16 grms. of benzene are collected on distillation. The contents of the flask, taken up with water, give an alkaline liquid which gives 45 grms. of benzoic acid by acidification with a dilute acid. Now, if the above alkaline liquor is washed with ether before the addition of the dilute acid, an ethereal solution is formed, which on evaporation leaves 25 grms. of a solid product. After crystallisation in alcohol at 80° , this compound fuses at 159° , and possesses all the properties of triphenylcarbinol.

Solid Azotic Colouring Matters derived from a-Aminoanthraquinone.—C. Lauth.—Already noticed.

Sparteine; General Characteristics.—C. Moureu and A. Valeur.—Already noticed.

Sparteine; Action of Some Reducing Agents.—C. Moureu and A. Valeur.—Already noticed.

Examination of some Ancient Breads.—L. Lindet.—Already inserted in full.

PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN that NOBERT CRIPEK, of 5, Matzleinsdorfstrasse, Vienna, V., in the Empire of Austria, seeks to amend the Specification of Letters Patent No. 21627 of 1900 granted to him for "IMPROVEMENTS IN EXPLOSIVE COMPOUNDS."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents) issued on July 6th, 1904.

Any person, or persons, may give Notice of Opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

C. N. DALTON,
Comptroller-General.

ABEL and IMRAY,
Consulting Engineers and Chartered Patent Agents,
Birkbeck Bank Chambers, Southampton Buildings,
London, W.C.
Agents for the Applicant.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.
LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.

RADIUM

ON SALE AND LET ON HIRE.—Write for terms.

The following can be had by return of post.

Pitchblende, direct from Joachimsthal, very radio-active, from 1/- to 30/- per piece.
Itacolomite, or flexible sandstone, 10/- to 25/- per piece (very rare).
Kunzite, 1/- per gramme. Selected, clear, 2/-
Spartite (see NATURE, 31/3/04, fol. 523), 2/- and upwards.
Chlorophane, 2/- and upwards. Barium Platino Cyanide in large Crystals in course of manufacture. (ORDERS BOOKED).
Zinc Sulphide. Phosphorescing a beautiful Green, 2/6 per tube.
" " " Yellow, 2/8 " "
Calcium Sulphide " " Violet, 1/- " "
Radio-active Residue from which Radium is made; very scarce, 2/ tube.
Polonium Sulphide, in tubes of one gramme, 21/-
" on Bismuth Rod or Disc, ... 25/-
" on Copper " " 25/-
Radio-active Screens (Willemite), 8d. per sq. inch. Plat. Bar. Cyan Screen, 9d. sq. inch.
" " (Zinc Sulphide), 10 x 10 cm. 7/6.

Professional Men, Universities, Schools, &c., allowed special terms

Our newly invented Thorium Inhalers may be had on hire.

ARMBRECHT, NELSON & CO.,

71 & 73 DUKE ST., GROSVENOR SQ., LONDON, W.

Telephone: GERRARD 4942.

N.B.—We have to-day received a consignment of the New Zealand Vegetable Caterpillar; it is from 2 to 3 inches long, with a stem showing fructification growing out of its head. Scientific name of the insect is *Hepialus virescens*; the name of the fungus is *Sphaeria Robertiana*. Specimens may be had from 10/6 to 21/-, according to quality and size.

TERMS CASH WITH ORDER.

Goods may be returned if not approved of, when money will be refunded.

E. GEORGE & SONS,
BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.

Are OPEN to PURCHASE Complete Sets

or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.

BRYAN CORCORAN Ltd.

MILLSTONE BUILDERS,
WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.

Sole Makers of MILBURN'S
Patent Conoidal Stone Grinding Mills.
Especially suitable for certain materials, Wet or Dry.

Works and Warehouses: Back Church Lane,
Parcel Dept.: Basement of the Corn Exchange,
31, MARK LANE, LONDON.

ST. PAUL'S SCHOOL, West Kensington.—

An EXAMINATION will be held at the above School on Tuesday, September 6th, 1904, and on the following days, for filling up about Twenty Vacancies on the Foundation.—Full particulars of the Examination can be obtained on application to the Bursar.

SHELLAC PATENT, No. 4550.

LICENSEE for ENGLAND, eventually
also for the UNITED STATES OF AMERICA, Patent
No. 760541, FOR SALE. High profit. Approved proceeding for
Varnishes, Polish, Hat Manufacture, Sealing-wax, Finish, &c.

For particulars apply to CARL CORDES, MAGDEBURG, GERMANY.

THE CHEMICAL NEWS.

Vol. XC., No. 2330.

THE ATOMIC WEIGHT OF TUNGSTEN.*

By EDGAR F. SMITH and FRANZ F. EXNER.

Literature.

BERZELIUS, *Pogg. Ann.*, 1826, viii., 1; Schneider, *Journ. Prakt. Chem.*, 1850, l., 152; Marchand, *Ann. Chem. Pharm.*, 1851, lxxvii., 261; Borch, 1851, *Journ. Prakt. Chem.*, liv., 254; Riche, *Journ. Prakt. Chem.*, 1857, lxxix., 10; Dumas, *Ann. Chem. Pharm.*, 1860, cxiii., 23; Bernoulli, *Pogg. Ann.*, 1860, cxl., 573; Scheibler, *Journ. Prakt. Chem.*, 1861, lxxviii., 324; Roscoe, *Ann. Chem. Pharm.*, 1872, cxli., 368; Waddell, *Am. Chem. Journ.*, 1886, viii., 280; Pennington and Smith, *Zeit. f. Anorg. Chem.*, 1895, viii., 198; Smith and Desi, *Zeit. f. Anorg. Chem.*, 1895, viii., 205; Shinn, Thesis, University Pennsylvania, 1896; Schneider, *Journ. Prakt. Chem.*, 1896, liii., 283; Hardin, *Journ. Am. Chem. Soc.*, 1897, xix., 657; *Ibid.*, 1899, xxi., 1017; Thomas, *Journ. Am. Chem. Soc.*, 1899, xxi., 373; Taylor, Thesis, University of Pennsylvania, 1901.

The literature pertaining to this subject covers a period of nearly three-quarters of a century. Eight different methods have been used in striving to solve the problem. They are:—

1. Reduction of Tungsten Trioxide.—Berzelius, 2; Schneider, 5; Marchand, 2; Borch, 7; Dumas, 8; Bernoulli, 6; Persoz, 2; Roscoe, 3; Waddell, 5; Schneider, 3; Shinn, 4; Hardin, 29. A total of 78 reductions.
2. Oxidation of Metal.—Schneider, 3; Marchand, 2; Borch, 2; Bernoulli, 4; Roscoe, 2; Pennington and Smith, 9; Schneider, 3; Hardin, 37. A total of 62 oxidations.
3. Weighing the Water from the Reduction of Trioxide.—Riche, 2; Smith and Desi, 6.
4. Determination of the Water Content of Barium Metatungstate.—Scheibler, 5; Hardin, 2.
5. Analysis of Tungsten Hexachloride.—Roscoe, 2.
6. Analysis of Iron Tungstate.—Zettnow, 4.
7. Analysis of Silver Tungstate.—Zettnow.
8. Determination of the Water in Sodium Tungstate.—Thomas, 22.

The results obtained by the first and second methods are the most numerous. The frequent employment of these methods would indicate the opinion to be general that they are the most rational. This they are, notwithstanding the want of concordance evident in the work of all chemists who have pursued either one of these methods in the attempt to solve the existing problem. Their sufficiency has been doubted, especially by Hardin, working in this laboratory. He was disposed to attribute the lack of agreement in his work to volatilisation of substance, both in the experiments of reduction of trioxide and in those in which the metal had been oxidised. Hardin adopted the method of purification pursued by Pennington and Smith, and therefore believed that the material with which he operated was pure; hence the errors were the result of imperfections in the method employed.

Pennington and Smith, cognisant of the presence of molybdenum in the tungsten compounds, confirmed by numerous observations of others, were induced to undertake a solution of the difficulty surrounding the atomic weight of tungsten because they noticed in Schneider's communication, that when he reduced tungsten trioxide in a

current of hydrogen "ein weissliches Sublimat" appeared on the anterior portion of the reduction tube, which sublimate Schneider thought was tungsten chloride, but which Pennington and Smith, in the light of the discovery of molybdenum in all tungstates, believed was due to the latter element. They accordingly purified a portion of tungsten trioxide by the plan recommended by Schneider, and, after eliminating any possible molybdenum content, made tungsten metal and oxidised it. They gave as a result of their labours probably the most concordant series of figures ever published for the constant in question. The other striking feature of this series was their high value, namely, 184.92. This was much higher than that generally considered to be the correct value. Its rise was supposed to be due to the complete removal of molybdenum. Let it be noted that Pennington and Smith used tungsten metal from trioxide reduced in a crucible of platinum, and further that they used the second method only.

The work of Smith and Desi, who used the third method, apparently confirmed the conclusions of Pennington and Smith. It may be said that the early work of Schneider, leading to the value 184, had been practically confirmed by subsequent investigators, so that the constant 184 had been looked upon for a period of forty-five years as the accepted atomic weight of tungsten. The experiments of Pennington, Smith, and Desi could not fail to be regarded with some question notwithstanding the evident care exercised by them in preparing suitable material for their respective studies, and the conscientiousness to detail exhibited in the experimental work. Schneider was still living on the appearance of the communications just referred to, and in letters to one of us, as well as in a public print, naturally took exception, in the most courteous manner, to the methods and to the conclusions of those who advocated the higher value (184.92). It is not necessary here to enter into a detailed review of Schneider's second and later paper. Briefly, he very much doubted whether it was the complete removal of any molybdenum content from the tungstic acid which occasioned the rise in the atomic number. He also entertained grave doubts as to whether, in the methods employed, there were not sources of error which escaped these chemists. The small quantities of material used by Pennington, Smith, and Desi were, in the opinion of Schneider, contributory sources of error.

The problem, attracting new attention to itself in this laboratory, led to further studies upon this subject, chief among which were the painstaking investigations of Hardin, extending over several years. Reference to these will show that few points of inquiry escaped this investigator, and one can readily comprehend the spirit which prompted him to say in his final contribution on this subject:—

"So far as known there is no perfectly reliable method for the determination of this constant. The method of reduction and oxidation is probably more accurate than any of the other methods which have been employed. The results obtained by it vary about one unit and even more in exceptional cases."

In our frequent discussions on this topic, it did seem as if search for new methods was absolutely required; that these alone might be expected to settle the difficulty once for all. Taylor, engaged at the time in this laboratory upon the ammonium tungstates, noticed that ignited tungsten trioxide, when dissolved in a solution of pure sodium carbonate, left a white flocculent residue. When dissolved in potassium hydroxide, this residue was not so evident, and in his thesis (University of Pennsylvania, 1901) he continues:—

"On standing a few hours in sodium carbonate, this residue turned reddish-brown. On treatment with hot concentrated hydrochloric acid, it (having been previously washed) broke down into tungstic acid, and the filtrate contained the chlorides of iron and manganese. To ascertain if the original ammonium tungstate would reveal the presence of these impurities, it was dissolved in water, feebly acidulated with hydrochloric acid, and ammonium sulphocyanate added. No coloration was produced.

* From *Proceedings of the American Philosophical Society*, vol. xliii., No. 176.

Another portion of the solution was boiled with hydrochloric acid, the tungstic acid precipitated, and now the filtrate easily showed the presence of iron.

"The residue, insoluble in sodium carbonate, appears to be a tungstate of iron and manganese, which probably existed in the ammonium salt, as an ammonium iron-manganese tungstate. Laurent states that the mother-liquor from ammonium tungstate contains such a salt (*Journ. Prakt. Chem.*, 1847, xlii., 126). He ascribed to it the formula $12(\text{NH}_4)_2\text{O} \cdot 6\text{MnO}_2 \cdot 2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \cdot 45\text{WO}_3 \cdot 8\text{H}_2\text{O}$ (*Comptes Rendus*, 1850, xxxi., 693).

"Borch analysed this salt with the following results (*Journ. Prakt. Chem.*, 1851, liv., 254):— WO_3 84.4 per cent, $(\text{Fe}_2\text{O}_3 + \text{Mn}_2\text{O}_3)$ 4.6 per cent, NH_3 4.0 per cent, H_2O 7 per cent. Laurent states that this complex salt is soluble in water and ammonia, and is peculiar in that ordinary reagents do not show the presence of iron, manganese, or tungstic acid; further, that the salt is only broken down by prolonged boiling in acids or alkalis, and then the ingredients can be readily detected.

"Schneider recognised the presence of this salt in ammonium tungstate, and stated that it was not removed after five or six re-crystallisations (*Journ. Prakt. Chem.*, 1850, l., 152). Also that it could not be removed by the ammonium sulphide treatment, for slight amounts of the sulphides of iron and manganese are soluble in the tungsten sulpho-salt. Berzelius stated that the sulphides of tungsten, iron, and manganese form a compound which is partly soluble in water (*Pogg. Ann.*, 1826, viii., 279).

"To remove this complex salt, Schneider purified his material in the following way:—Tungstic acid, obtained from the sulpho-salt of tungsten, was boiled in aqua regia, and washed in acidulated water till free from iron. This was dissolved in dilute ammonia, and the solution precipitated by boiling hydrochloric acid, the resulting tungstic acid boiled in aqua regia, and again washed. This oxide was again dissolved in ammonia, and again precipitated. After re-precipitating three times in this manner, tungsten trioxide was obtained free from iron. However, on dissolving the oxide in potassium hydroxide, a slight brown residue remained which had escaped all earlier tests. This he assumed was not enough to affect the result of his work.

"Had he applied the sodium carbonate test, this residue would have been larger. In the recent repetition of his work (*Journ. Prakt. Chem.*, 1896, cli., 288), he used material purified in precisely the same manner (in fact some of the original material), with the exception of the treatment for the elimination of molybdic acid.

"Borch recognised this complex salt, and tried to remove it by fusion with potassium carbonate (*Journ. Prakt. Chem.*, 1851, liv., 254).

"Later investigators seem not to have appreciated the difficulty of eliminating it. It crystallises in part with the ammonium tungstate, and can scarcely be entirely removed by re-crystallisation. Ignition of the ammonium salt, and resolution in ammonium hydroxide will not eliminate it. Nor will ammonium sulphide remove it. In fact, it seems likely that it has never been wholly extracted from any previous material.

"The purification by Pennington and Smith did not remove it (*Proc. Amer. Phil. Soc.*, 1894, xxxiii., 332), for though closely following the method outlined by Schneider, and adding to it the complete elimination of molybdenum, they omitted the final repeated precipitations with acid.

"To understand the effect of possible impurity, the following table is given. A molecular mixture of tungsten and the impurity is treated as though it were all tungsten, and the resulting atomic weight calculated.

Molecular mixture.	Reduction series atomic weight.	Oxidation series atomic weight.
W + W	184	184
W + Mo	140	140
W + 2Fe	148	148
W + 3MnO	298	298
Loss of material	Low	High

"A consideration of these numbers shows that molybdenum and iron would produce a low value; manganese a high value; volatility a low value on reduction, and a high value on oxidation. The error introduced by manganese is more than three times as costly as that introduced by iron, and more than two and a half times that introduced by molybdenum. These ratios would apply regardless of the proportion of the mixture.

"From these considerations it is believed, that the presence of manganese and iron will account for the high oxidation values, for their presence would affect the result in a twofold manner:—Manganese through its inherent molecular changes, $\text{Mn}_2\text{O}_3 \rightleftharpoons \text{MnO}$, and iron through its secondary action on the volatility. Further, that the presence of iron, molybdenum, manganese, and volatility will explain the numerous discrepancies noted in the published work on this subject. Again, since iron and molybdenum decrease the value, and manganese and volatility increase the value, and iron and molybdenum influence the volatility, it is quite possible that such a mixture of these factors might occur that the errors would be compensated.

"Viewed in this way there still remains the necessity for determinations with material from which every trace of molybdenum, iron, and manganese, together with other possible impurities, has been removed.

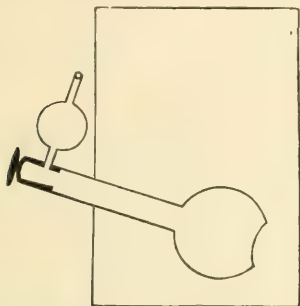
"The method of determining atomic weights from the loss of carbon dioxide has been applied to a number of the elements. Its application to tungsten, and the special modification of the method necessary for accurate determinations, has not been before recorded. Svanberg and Struve fused molybdenum trioxide with potassium carbonate and determined the loss in weight (*Journ. Prakt. Chem.*, 1848, xlv., 301). Their value is nearly six units too low, and the method must be considered inaccurate. This method was tried with tungsten trioxide, and gave values ranging from 160 to 180. The disadvantages of the method are that the union takes place with considerable spattering; the temperature of fusion is so high that loss by volatility is probable; the alkaline carbonates when held in fusion slowly lose traces of carbon dioxide; and the resulting fusion is extremely hygroscopic.

"These difficulties may be obviated by combining the oxide and sodium carbonate in aqueous solution, and then expelling the water. Operated in this manner the method possesses promising value; and has numerous advantages, among which may be mentioned that carbon dioxide has a molecular weight of forty-four, giving a value for comparison nearly as great as in the simple reduction and oxidation method; the union of sodium carbonate and tungsten trioxide in aqueous solution takes place at a low temperature, and the highest temperature used in the desiccator is a safe distance below the melting-point of sodium carbonate, so that there is little chance for volatilisation either of sodium carbonate or tungsten trioxide, and in the device used there is no chance for loss by spattering; large quantities of material may be combined with as much ease as small; the method itself would serve for a test of the purity of the material; the presence of chlorides, sulphates, sodium silicate, and potassium carbonate would not affect the result. The presence of alkaline hydroxides would; and to prevent the possibility of this, pure sodium carbonate was saturated in solution with carbon dioxide, and the resulting bicarbonate heated in a vacuum at 300° for three hours.

"The tungsten trioxide and sodium carbonate were combined in a glass bulb as in the sketch. A neutral glass is desirable for this purpose, and the bulb should be made of Jena glass, which will withstand the action of alkaline carbonates better than ordinary glass. If sodium carbonate dissolves the glass no error will be introduced, but if carbon dioxide be liberated through such solution, then the glass cannot be used. To determine this point a blank experiment was made, which showed that the total weight of the bulb and sodium carbonate remained unchanged, while 0.007 grm. of glass were dissolved; hence no appreciable evolution of carbon dioxide occurred. How-

ever, to prevent any possibility of such loss, a platinum bulb had better be used.

"It was found that moist sodium carbonate could be heated to a constant weight, by heating for one and a-half hours at a temperature of 300° in a vacuum; and in this bulb the weight after standing several days remained unchanged. To insure complete desiccation the bulb was always heated double the required length of time. A water pump was used to produce the diminished pressure, and since nothing can be perfectly dried in a vacuum resulting from such a pump, a calcium chloride tower was introduced. But calcium chloride will not perfectly desiccate a gas, so that phosphorus pentoxide had better be used. However, for the preliminary experiments in hand, calcium chloride was sufficient.



"The method of procedure was as follows:—Some sodium carbonate was introduced into the bulb and heated for three hours at 300° in a vacuum. The suction was disconnected, and after cooling, the combined weight of bulb, sodium carbonate, and dry air was obtained. Tungsten trioxide was then introduced through a long funnel, the bulb was exhausted, allowed to fill with dry air, and again weighed. This gave the weight of tungsten trioxide. The weight of the sodium carbonate, further than being present in excess, need not be known. Water was added, and the bulb heated in a glass air-bath, so that the course of the reaction could be watched. The mixture slowly effervesced, and when the action had ceased, the vacuum apparatus was attached, and the water distilled off. This water was tested and found to be neutral. The calcium chloride tower was now introduced, and the residue, consisting of a mixture of sodium tungstate and carbonate, was heated for three hours at 300° in a vacuum. After cooling, and thus allowing the bulb to fill with dry air, it was detached and weighed. This loss in weight gave the carbon dioxide evolved. It may be added that the entire bulb should be inside the air-bath, until the water has been removed; and then the upper portion be placed outside, and the temperature increased to 300° . In this way no moisture will condense in the head, and the stopper remaining perfectly dry will not become jammed. The stopper should not be lubricated.

"The following results were obtained, from impure material, which in the previous experiments in this paper gave values ranging from 182.24 to 184.82 , and which was known to contain iron, manganese, and probably molybdc acid:—

Weight of Na_2CO_3	Weight of WO_3	Weight of CO_2	Atomic weight of tungsten.
Grms.	Grms.	Grm.	
1... 2.7	2.0802	0.3952	183.60
2... 2.3	2.1937	0.4173	183.30
3... 3.5	3.0818	0.7762	183.38
4... 3.8	3.3629	0.6394	183.41

"These numbers, in that they indicate the atomic weight of tungsten, are worthless; in that they show promise for the new method, are of value. The presence of impurity would lower the result; what value the method will give for pure material can only be conjectured."

(To be continued).

THE CONSTITUTION OF THE AMMONIUM COMPOUNDS.*

By JOHN CANNELL CAIN, D.Sc., M.Sc.

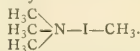
THE theory of ammonium compounds, proposed by Ampère in 1816 and generally accepted even at the present time, has not, in spite of its continuance, been entirely free from attack.

The objections of Kekulé, based on his non-belief in the existence of a pentad nitrogen atom, cannot, of course, be regarded as valid to-day, as the doctrine of variable valency is everywhere accepted.

Thus Japp, in the Kekulé Memorial Lecture, 1897, says, "the doctrine . . . of fixed valency . . . is, so far as I am aware, without supporters."

We have long given up, therefore, Kekulé's molecular formula of ammonium chloride, $\text{NH}_3\cdot\text{HCl}$, although we still adhere to this method of writing a large number of so-called molecular compounds.

The difficulty of explaining the union of ammonia and hydrochloric acid in terms of the ammonium theory was raised by Chevreul, and Wurtz ("The Atomic Theory," 1880) found it hard to explain why the chlorine should give up its affinity for hydrogen, and unite with nitrogen for which it has only a slight attraction. He pointed out that, although the separation of chlorine and hydrogen should give rise to a considerable absorption of heat, and the union of chlorine and nitrogen can produce only a feeble evolution of heat, yet the formation of sal-ammoniac gives rise to a considerable evolution of heat. Wurtz's explanation of this is that "the affinity of the chlorine for hydrogen is satisfied by the attraction which it exercises upon all the atoms of hydrogen within the sphere of which it is now situated." This, however, goes beyond the confines of the valency theory. The inability of the ammonium theory to explain the extraordinary stability of tetramethyl ammonium iodide to caustic potash has been pointed out by Armstrong in 1888 (*Phil. Mag.*, [5], xcv., 21), and also in his article "Chemistry" in the *Encyclopædia Britannica*. He says, "It is highly remarkable that tetramethyl ammonium iodide should not be in the least affected by even the strongest caustic alkali, and that the halogen . . . behaves much as does that in alkylic haloids. This would seem to be a strong argument in favour of the view that the halogen is not simply associated with the nitrogen, but retained in combination with the hydrocarbon radicle." Armstrong suggested (1888) that this substance should be represented by his "residual affinity" formula—



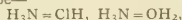
An important objection to the ammonium theory has quite recently arisen in the existence of isomeric optically inactive organic ammonium salts. Werner (*Annalen*, 1902, cccxxi., 261) instances the two isomeric trimethyl isobutyl ammonium salts of Le Bel (*Comptes Rendus*, cx., 144), the two methyl di-ethyl amyl ammonium chlorides of Schryver (*CHEMICAL NEWS*, 1891, lxi., 174), and the ethylene propylene dipiperidinum bromides of Aschan (*Ber.*, 1899, xxxii., 988). Aschan, however, has contradicted the existence of the latter (*Ber.*, 1903, xxxvi., 1164), and the other two cases may be attributed to dimorphism (compare Jones, *Journ. Chem. Soc.*, 1903, lxxxiii., 1401).

* From the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, 1904, xlviii., No. 14.

There are still the isomeric inactive phenyl, benzyl, allyl, methyl ammonium iodides of Wedekind (*Ber.*, 1899, xxxii., 518), one of which has been resolved into its optically active constituents by Pope and Peachey (*Journ. Chem. Soc.*, 1899, lxxv., 1127), and the several sets of isomers described by Kipping (*Journ. Chem. Soc.*, 1900, lxxvii., 861; 1901, lxxix., 430; 1903, lxxxiii., 873), which are well defined. The latter has obtained two isomers of hydriindamine bromocamphorsulphonate, chlorocamphorsulphonate, and *cis-r*-camphanate, as well as others from substituted hydriindamines, none of which contain an asymmetric nitrogen atom. The existence of such isomeric forms recalls the experiments of V. Meyer and Lecco (1876), who showed the identity of the quaternary ammonium iodides obtained from trimethylamine and ethyl iodide, and ethyl dimethylamine and methyl iodide, and concluded that this compound was properly represented by the ammonium theory, and not to be regarded as a substituted ammonia hydrochloride. This conclusion must now be doubted in view of the many cases of two isomers here quoted.

Werner proposes a new ammonium theory, which—involving as it does, such terms as “principal valency” (“hauptvalenz”), “supplementary valency” (“nebenvalenz”), and “co-ordination constant”—is apparently not very different from the older idea of molecular attraction or residual affinity. According to Werner, the formula of ammonium chloride would be $H_3N \cdots HCl$, a supplementary valency (indicated by the dotted line) existing between the nitrogen atom and the hydrogen of the hydrochloric acid—an assumption for which there is at present no experimental evidence.

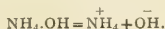
The constitution which I suggest for the ammonium compounds would, I believe, account in a very simple manner for the whole of the facts referred to above, and the formulæ for ammonium chloride and ammonium hydrate would be—



in which chlorine is triad and oxygen tetrad. The statement that, in the case of a pentavalent nitrogen atom, only four valencies can attach themselves to an organic radical, the fifth being always united to a halogen or hydroxyl group (compare Vaubel, “Stereochemische Forschungen,” 1899; Wedekind, “Zur Stereochemie des fünf wertigen Stickstoffes,” 1899) is at once explained in the light of this formula. It is perhaps hardly necessary to adduce evidence in favour of the conception of triad chlorine. Thus Armstrong writes (“*Encycl. Brit.*,” *loc. cit.*):—“As it is clear that iodine may exercise triadic functions, the remaining halogens can scarcely be denied the rank of potential triads.” And, again, Ramsay says (“*Modern Chemistry*”):—“It must . . . be assumed that the halogen atoms are . . . possibly triads. The mode of combination of these double salts (*i.e.*, $ZnCl_2 \cdot 2KCl$) is possibly owing to the fact that the halogens are capable of acting as triads.” That oxygen can often become tetravalent is to-day generally accepted.

(NOTE.—Although, as I find, these formulæ occur, together with corresponding ones for tetramethylammonium iodide and tetraethylphosphonium iodide in a paper by Heyes on Valency (*Phil. Mag.*, 1888, [5], xxv., 297), yet no arguments are used in favour of them, and no further application of them is made).

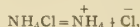
The union of ammonia and hydrochloric acid is very simply explained by the equation $H_3N + ClH \rightarrow H_3N = ClH$. The influence of moisture on this combination is, in my opinion, the same as in the case of the union of carbon monoxide and oxygen where there is no question of ionisation, or possibly intermediate addition compounds are formed with water by both ammonia and hydrochloric acid. The electrolytic dissociation of sal-ammoniac and ammonium hydrate is quite in accordance with the new formula. Whereas according to the usual ammonium theory, ammonium hydrate should dissociate in the same way as potassium hydrate,—



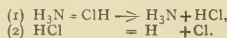
As a matter of fact the degree of dissociation is exceedingly small, resembling that of water, and Hantzsch has shown that the dissociation takes place in the sense that water is split off (*Zeit. für Phys. Chem.*, xxx., 258). This is to be expected if we write—



The almost complete electrolytic dissociation of sal-ammoniac in dilute solution is equally well explained by both theories; thus we have—



and—



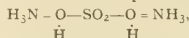
We get here a complex ion, $NH_3.H^+$, and there is, of course, no evidence as yet which can decide between the

ion NH_4^+ and the more complex one $NH_3.H^+$.

The remaining halogen salts of ammonia are analogously written, and the sulphides thus:—



My formula for ammonium hydrate, $H_3N = OH_2$, is analogous to that of water, $H_2O = OH_2$; of hydrogen peroxide, $O = OH_2$; and of ozone, $O = O = O$. The general formula for salts of ammonia and oxygen acids is $H_3N = OHX$; thus ammonium sulphate is written—



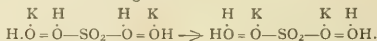
oxygen, of course, being tetrad.

The obvious question as to the possibility of this formula, in view of the isomorphism of the ammonium and potassium salts, at once arises. Ought we not, however, to expect some difference between these salts from the fact that water is always eliminated in the formation of, for instance, potassium sulphate, while no such reaction takes place in the case of ammonium sulphate? The formation of potassium sulphate may, however, be exactly analogous to that of ammonium sulphate. Thus:—

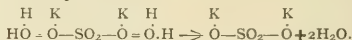
1. Addition—



2. Molecular change—

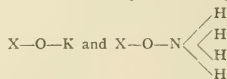


3. Water split off—

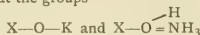


In the case of ammonium sulphate, the group attached to the tetrad oxygen atom is split off at a higher temperature.

If we have hitherto regarded as isomorphous, compounds containing two such differently constituted groups as—



can we say that the groups—



would not belong to isomorphous salts.

Lothar Meyer says (“*Outlines of Theoretical Chemistry*”) “it has been assumed that an atom of potassium can be isomorphously replaced by the ‘compound radical’ ammonium, composed of one atom of nitrogen and four atoms of hydrogen; but if this is possible in one case, it may

frequently happen that several atoms replace one single atom. If we admit this, then the whole foundation of these considerations (i.e., on isomorphism) is weakened (the italics are mine). We must also not forget that the nitrates, the bichromates, and the persulphates of potassium and ammonium are not isomorphous. There is thus no argument from the theory of isomorphism which negatives my view.

(To be continued).

ESTIMATION OF THE PERCHLORATE OF SODIUM IN COMMERCIAL NITRATE OF SODIUM.

By H. LEMAITRE.

It is the usual custom to sell nitrate of sodium for commercial uses at so much per cent of nitrate of sodium determined by difference, and at a maximum proportion of 0.37 to 0.57 of chlorine according to agreement. In the "commercial" analysis the following estimations are made:—Moisture, insoluble residue, sulphate, and chloride of sodium. No mention is made of the perchlorate or of the iodate of sodium, although seven or eight years ago the attention of chemists and manufacturers was drawn to the never negligible, and sometimes high, proportion of perchlorate (rarely iodate) present in saltpetres from Chili.

However, besides the fact that the presence of these bodies vitiates the commercial analysis, as is admitted, the perchlorate and the iodate in similar proportions are as objectionable as chloride of sodium in the principal commercial uses of the Chili nitrates.

We know that chlorine is an important factor in the destruction of the lead chambers, and, on the other hand, manufacturers of explosives who use large quantities of nitrates require nitric acid with a very small proportion of chlorine.

Therefore it would be more rational to value the chloride, perchlorate, and iodate of a saltpetre as chlorine, and also if we wish to establish the percentage of pure nitrate by difference to take note of the presence of the perchlorate and iodate.

In the meantime we give a new method for the estimation of the perchlorate.

This estimation is based on the following reaction:— $\text{ClO}_4\text{Na} + (\text{SO}_3\text{Na}_2)_1 = (\text{SO}_3\text{Na}_2)_1 + \text{NaCl}$. For a nitrate containing less than 4 per cent of perchlorate the proportions are:—

Chili saltpetre 5 grms.
Pure dry sulphite of sodium 3 "

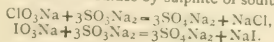
The sulphite and the nitrate are mixed in the dry powdered state, and placed in a platinum crucible. Heat carefully until the mass is in tranquil fusion. Allow to cool, and take up with water.

The solution is then boiled, and 200 c.c. of a boiling solution of nitrate of barium at 4 per cent is poured in. The precipitate is allowed to settle, and filtered.

The solution, treated with about 8.2 c.c. of normal soda, then with 1.2 gm. of persulphate of sodium, is brought to boiling, and filtered. The clear solution, added to the wash waters, is slightly alkaline. It is neutralised exactly with a dilute solution of acetic acid, using phenolphthalein as an indicator. Titrate with N/10 nitrate of silver, using chromate of potash as the indicator.

The proportion of chlorine can be also determined by weighing the chloride of silver precipitated by the decinormal nitrate of silver.

The chlorates and iodates are equally reduced to the state of chlorides and iodides by sulphite of sodium:—



The treatment with sulphite of sodium should therefore have the result of bringing to the state of chloride and iodide all the perchlorate and iodate of sodium contained in Chili saltpetres.

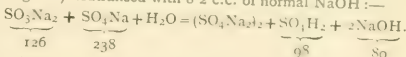
The iodate can be estimated by M. Auzenat's colorimetric method (*Moniteur Scientifique*, February, 1900).

The chloride and iodate of sodium are estimated directly on the nitrate of sodium by means of an excess of decinormal solution of nitrate of silver.

It is easy then to calculate the percentage of perchlorate.

Note.—The nitrates used for the manufacture of nitric acid generally contain less than 2 per cent of perchlorate and iodate; in any case, if the estimation gives more than 4 per cent we ought to begin again on 5 grms. of the nitrate, doubling the amounts of the reagents used. Five grms. of nitrate at 4 per cent = 200 m.grms. of ClO_4Na , for which theoretically we ought to use 82.3 m.grms. of pure SO_3Na_2 . Actually we use 3 grms. of SO_3Na_2 .

Three grms. of sulphite of soda, or their equivalent in SO_3Na_2 , are precipitated by 6.214 grms. of NO Ba. We use 200 c.c. at 4 per cent, that is 8 grms. : 8 grms. : 6.214 = 1.786 of NO_3Ba , corresponding to 0.814 of SO_3Na . We use 1.2 grms. of persulphate of soda (at 71 per cent = 851 m.grms.) neutralised with 8.2 c.c. of normal NaOH:—



—*Moniteur Scientifique*, Series 4, vol. xviii., April, 1904.

THE TRANSFORMATION OF THERMOCHEMICAL ENERGY INTO VOLTAIC ENERGY OR ELECTROMOTIVE FORCE.*

By D. TOMMASI.

Of late years a number of papers have been published on two-fluid batteries which exercise a reciprocal chemical action (action of a base on an acid, for example); this has rendered possible the observation that the nature of the electrodes plays a very important part in the amount of electromotive force developed by these batteries.

Thus, with uncomposable electrodes we observe that the electromotive forces of certain voltaic couples are often different from the electromotive forces calculated from the heat of the reactions, and, further, that they differ among themselves for the same liquids, according to the nature of the metals which constitute the electrodes of these couples.

These facts, though looked upon as new, were, however, observed and described by me in 1882 in a paper I presented to the Académie des Sciences, (*Comptes Rendus*, June 5, 1882) entitled "Influence of the Positive Pole of a Battery on the Quantity of Heat Transmissible to the Circuit in the form of Voltaic Energy."

In this paper I remarked that, contrary to the accepted opinion, the electromotive force of a definite voltaic couple varies according to whether its positive electrode consists of an unattainable metal or of carbon.

Such a couple, for example, that is incapable of effecting the electrolysis of water,† or of a saline solution, although the heat given off by the couple is greater than the heat observed in the electrolyte, if its positive electrode (that is, the electrode of the voltaic couple) is of platinum, copper, or silver, becomes apt to produce this decomposition if its positive electrode is of carbon. The following is an

* Thermochemical energy is that which can be observed and measured by means of a thermometer, it is the energy produced in most batteries by the action of zinc on dilute sulphuric acid. = *Free energy*, or electromotive force, is the energy capable of causing electrolytic decomposition, without the power, however, of furnishing the energy necessary for the liberation of ions.

† The apparatus used for the electrolysis of water, or the voltammeter, consisted of a glass vessel filled with acidulated water and into which two electrodes of platinum wire were plunged.

example:—A mixed chromic and sulphuric acid couple* should give, according to Favre, 117.3 calories (2.5 volts), but only 62.5 calories (1.35 volts) would be transmitted to the circuit. (See "Traité des Piles Electriques," by D. Tommasi, p. 6).

Thus it results that a single chromic acid couple should not decompose water acidulated with sulphuric acid. As a matter of fact, if the positive pole of this element is of platinum-foil the water in the voltmeter is not decomposed, but if the positive pole is of carbon or of platinum-sponge, the electrolysis of the water takes place.

The chemical reaction produced in the interior of the chromic acid couple being always the same, no matter what the nature of the positive electrode is, I have endeavoured to determine approximately by means of electrolysis what voltaic energy (electromotive force) is transmissible to the circuit by this couple when its positive electrode is of platinum, carbon, or platinum-sponge. The following are the results I obtained.

a. The chromic acid couple, such as I have already described, that is to say, with a platinum positive electrode, only produces a voltaic energy transmissible to the circuit of 1.4 volts corresponding to 65.5 calories.

b. By substituting carbon or platinum-sponge for the platinum-foil in this couple we can obtain about 85 calories (1.8 volts) transmissible to the circuit, or 20 calories (0.43 volt) more than the preceding couple.

What I have just said on the subject of the electrolysis of water applies equally well to the decomposition of saline solutions by the electric current.

In fact, I have found that two zinc-platinum and dilute sulphuric acid couples, connected in series, will not decompose a solution of sulphate of potassium.

Now, by using two zinc-carbon and dilute sulphuric acid couples, it is easy to decompose a solution of sulphate of potassium with the evolution of gas at both poles, and the passage of the acid to the positive pole and the base to the negative pole.†

The two experiments I have quoted prove in an unmistakable manner that the transformation of thermochemical energy into voltaic energy (electromotive force) is more complete with a positive electrode of carbon than with one of platinum-foil.

From what I have just described it follows that in all battery cells the thermochemical energy engendered by the soluble electrode (the zinc, for example) should be transformed into voltaic energy by the unattainable body (carbon or platinum) which forms the positive electrode.

This transformation of thermochemical energy into voltaic energy by the positive electrode would be total or partial according to the nature and the physical state of this electrode.

It might also very well be that the carbon plays the rôle of a transformer similar to the induction coil, and like the latter is capable of converting a quantity current into one of intensity.

If that be the case, the increase of the electromotive force, due to the substitution of carbon for platinum in certain voltaic couples, should be obtained at the expense of their respective capacities. In other terms, if the constants of a voltaic couple are, for example, 2 ampères and 1 volt, that is 2 watts, and if by the fact of substituting carbon for the platinum the electromotive force is increased to 1.5 volts, the capacity should be decreased to 1.33 ampères, so that 1.5 volts $\times$ 1.33 ampères = 2 watts.

We notice a still more strange occurrence with the magnesium-platinum and dilute sulphuric acid couple.

* This couple consists of an outer glass vessel containing an amalgamated zinc plunged into dilute sulphuric acid, and a porous pot containing 25 grms. of chromic acid, 50 c.c. of water, and 10 c.c. of sulphuric acid.

† The electromotive force necessary to decompose dissolved sulphate of potassium was found to be about 103 calories. As a matter of fact, there is no electrolysis under the influence of voltaic systems equivalent to 76 calories (1.63 volts), or even 98 calories (2 volts). On the other hand, there is electrolysis with the evolution of gas at the two poles with systems equivalent to 115.8 calories (2.5 volts) and even 103 calories (2.24 volts).

This couple consists of a magnesium wire and a platinum wire plunged together into dilute sulphuric acid. According to known thermic data, this couple ought to decompose water, since the heat given off by the action of magnesium on dilute sulphuric acid is greater than the heat absorbed by the decomposition of water. Actually 112.4 calories, the heat given off by the action of magnesium on sulphuric acid > 69 calories, the heat of the decomposition of water; still, as I have observed, the decomposition does not take place.*

The same is the case if we substitute copper or silver for the platinum in the magnesium cell. But if we use a cylinder of graphite or retort carbon for the positive pole in this element, the electrolysis of the water takes place.

According to Gore, the electromotive force of the magnesium-platinum and dilute sulphuric acid couple is 1.92 volts, corresponding to 85.3 calories, and consequently well over the heat of the decomposition of water (69 calories), and still, as we have seen, water is not decomposed.

Now, it has been always admitted that there is an equivalence between the voltaic energy transmissible to the circuit and the electromotive force of a cell; in other words, if the electromotive force of a couple is equal to 1 volt, for example, this couple will be able to bring about the decomposition of some definite compound of which the heat of decomposition is lower than 46 calories, corresponding to 1 volt. How is it, then, that in the magnesium couple we have an exception?

I will return before long to this important question, the solution of which will give not only a more satisfactory explanation of physico-chemical phenomena which take place in voltaic couples, but will show further the true rôle played by the nature of the positive electrode in the transformation of the thermochemical energy engendered by the attackable metal into voltaic energy or electromotive force transmissible to the circuit, and alone capable of bringing about a chemical decomposition.—*Moniteur Scientifique*, Series 4, vol. xviii., June, 1904.

PEROXYLAMINESULPHONIC ACID.

By EDWARD DIVERS, M.D., D.Sc., F.R.S.,
Emeritus Professor of Chemistry, Imperial University of Tokyo.

ALTHOUGH unrecorded in works on chemistry or chemical technology, it has long been known to inspectors and workers of the lead-chamber process for manufacturing sulphuric acid, that when, through improper working of the chambers, sulphur dioxide is allowed to pass into the Gay-Lussac tower, it produces with the nitrososulphuric acid, also present in the tower, what is called "purple acid," together with an effervescence due to the escape of nitric oxide (Carpenter and Linder, *J. Soc. Chem. Ind.*, 1902, xxi., 1492). Sabatier has shown (*Comptes Rendus*, 1896, cxviii., 147, 1479, and 1537; cxviii., 255) how to give an intensely bluish-violet colour, evidently the same as that of "purple acid," to the monohydrate of sulphuric acid holding nitrososulphuric acid in solution, either by passing sulphur dioxide into it, or by mixing it with sulphuric acid of similar strength containing dissolved

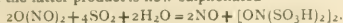
* True electrolysis must not be confounded with *electro pseudolysis*; that is to say, the separation effected by the current of the only products resulting from the dissociation of the electrolyte. Thus, to give only one example, with a dilute solution of chloride of ammonium with the help of a current of which the electromotive force is lower than that necessary for the decomposition of the salt, we can observe a distinct transportation of ammonia to the negative pole and of hydrochloric acid to the positive pole. But in this case we are not dealing with a true electrolysis but with an *electro-pseudolysis*, since the current has merely separated the only products of the dissociation of the dissolved chloride of ammonium. What I have just said of chloride of ammonium applies equally well to the decomposition of most salts, such as sulphate of potassium, acetate of sodium, the cyanides, formates, &c., for example. It is the same with the decomposition of water effected with a current of which the electromotive force is much lower than 1.5 volts (0.01 volt, for example).

sulphur dioxide. Such a sulphuric acid solution of sulphur dioxide may also be treated for some time with a current of nitric oxide and air; or, excluding air, the nitric oxide alone will produce the colour, when a very small quantity of either copper sulphate or ferric or ferrous sulphate has been previously dissolved in the acid. Lastly, certain metals and other substances serve to produce this colour, or a modification of it, by acting on nitrososulphuric acid in monohydrated sulphuric acid, among them being finely divided copper, silver, or mercury. Sabatier has not isolated the substance which gives this violet colour to sulphuric acid treated by the foregoing processes, but has suggested that it may be the unknown acid of Fremy's *sulphazilate*, which he re-names *nitrosodisulphonic acid*.

Now, in a preceding paper on peroxylaminesulphonates, Haga has adduced reasons for doubting the correctness of Sabatier's suggestion that the bluish-violet acid is sulphazilic acid, that is, peroxylaminesulphonic acid. There is also one consideration which, although not mentioned by Haga, may nevertheless have affected his judgment. This is the fact that a substance which, according to Haga's most conclusive evidence, must be a peroxide, should be produced in the ways prescribed by Sabatier. But this difficulty and those raised by Haga all seem to disappear when the changes which give rise to the acid and the very different conditions for the production of the salt and of the acid are all more closely examined, and leave nothing in the way of accepting the view that this acid is peroxylaminesulphonic acid.

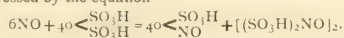
The fact that the violet acid is dissolved in sulphuric acid, whereas the violet salt is in aqueous solution, has to be taken into account when the differences in the behaviour of the two are under consideration. It will then be seen that these differences are really not greater than those between a sulphuric acid solution of nitrous acid (as nitrososulphuric acid) and an aqueous solution of potassium nitrite. The latter when acidified and the former when diluted both quickly lose most of the nitrous acid, there being no stable existence of this acid in the intermediate conditions. Potassium nitrite is unaffected by hydrogen peroxide or potassium permanganate, being, in fact, producible from nitric oxide by alkaline hydrogen peroxide (Carpenter and Linder, *loc. cit.*), and from hyponitrite by permanganate (Thum, *Monatsh.*, 1893, xiv., 294), whereas nitrous acid is converted by these reagents into nitric acid. Lead peroxide may therefore very well be active towards a sulphuric acid solution of peroxylaminesulphonic acid, although it does not interact with an aqueous solution of its salts. Again, that sulphur dioxide should not interact with peroxylaminesulphonic acid in presence of much sulphuric acid, and yet be very active towards a salt of the acid in water, may well be an instance of what indeed happens in case of mercuric oxy-salts, on which, in presence of much sulphuric acid, sulphur dioxide is no longer active (*Journ. Coll. Sci. Tokyo*, i., 106), or in that of ferric salts, which are very much more easily reduced by sulphur dioxide in the absence of sulphuric acid than in the presence of excess of it. Similarly, it may further be properly maintained that it does not follow that hydroxylaminetrisulphonic acid should be produced from peroxylaminesulphonic acid in sulphuric acid solution because its salt is produced in a neutral or an alkaline aqueous solution of a peroxylaminesulphonate. This contention being admitted, the non-formation of this acid, observed by Haga, is not significant.

Since the well-known compound, nitrososulphuric acid, is not a sulphonic derivative, as Sabatier takes it to be, but the mixed anhydride of nitrous and sulphuric acids, the nature of its conversion into the violet acid is easy to understand. Regarding the mixed anhydride as being simply nitrous anhydride (the sulphuric acid being undecomposed), the production from it of nitric oxide and peroxylaminesulphonic acid is seen to be only its usual decomposition into nitric oxide and nitric peroxide, except that the latter product is now sulphonated—



When metallic copper is used in place of sulphur dioxide, the generation of the necessary sulphur dioxide by the action of the metal on the pyrosulphuric acid of the nitrososulphuric acid only introduces an interesting complication. Pyrosulphuric acid at once interacts with copper in the cold (*J. Chem. Soc.*, 1885, xlvii., 638).

There remains to be considered the production of the "purple acid" along with nitrososulphuric acid from nitric oxide and sulphuric acid in the presence of cupric or ferric sulphate as a catalytic agent. The sulphuric acid being represented as existing in its pyro-state (the form in which it acts in presence of an oxide of nitrogen), the change is expressed by the equation—



As to the peroxidising action of sulphuric acid here shown, it may be well to recall the action of the acid upon metallic tin in presence of hydrochloric acid (Heumann and Koechlin, *Ber.*, 1882, xv., 420):—



In this equation the stannic chloride and the sulphur dioxide together take the place of the peroxylaminesulphonic acid in the previous one, for $[\text{ON}(\text{SO}_3\text{H})_2]_2$ can evidently be expanded into $\text{N}_2\text{O}_4 + 4\text{SO}_2 + 2\text{OH}_2$.

It is difficult to conceive of any other rational interpretations of Sabatier's remarkable results than those given above, and these are all consistent with the assumption that the purple acid is not merely isomeric, but actually identical with peroxylaminesulphonic acid, and is therefore a peroxide and an exclusively tervalent nitrogen compound.—*Journal College of Science, Imperial University, Tokyo*, xix., Art. 16.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1904.

By SIR WILLIAM CROOKES, F.R.S.,

and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,

Water Examiner, Metropolitan Water Act, 1871.

London, July 11th, 1904.

SIR,—We submit herewith, at the request of the Metropolitan Water Board and the Directors of the New River Company, the results of our analyses of the 203 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board and the New River Company taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 203 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford during the month of June has been considerably below the average, only 1.04 inch of rain having been recorded. The mean rainfall for June is 2.10 inches; thus we have a deficit of 1.06 inch, which, if deducted from the previous excess of 2.43 inches, leaves a total excess for the first six months of the year of 1.37 inches, or 12.6 per cent above the thirty-five years average.

Our bacteriological examinations of 384 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 380 others from special wells, standpipes, &c., making 764 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	112
New River, filtered (mean of 76 samples) ..	6
Thames, unfiltered (mean of 26 samples) ..	883
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 205 samples) ..	20
Ditto ditto highest	310
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	182
River Lea, from the East London Water Com- pany's clear-water wells (mean of 25 samples) ..	12

Of the 306 daily samples taken from the general filter wells of the Metropolitan Water Board and the New River Company, eighteen samples, or 6.0 per cent, were sterile. Nine samples, or 3.0 per cent, contained more than 100 microbes, and of these, two samples contained more than 150 microbes per c.c. The nine excess samples contained an average of 152 microbes per c.c. In May five excess samples contained an average of 143 microbes per c.c.

The results of the analyses show that the water distributed to London, under the direction of the Metropolitan Water Board and the New River Company, during the month of June has been efficiently stored and filtered; and that the high degree of purity recorded throughout the two previous months has been well maintained.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

NOTICES OF BOOKS

The Vegetable Alkaloids. By DR. AMÉ PICTET. Rendered into English from the Second French Edition by H. C. BIDDLE, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

This translation of Prof. Pictet's valuable treatise on the vegetable alkaloids will probably constitute the most complete text-book of its kind dealing with this subject in the language. The many advances which have been made during the last seven years have necessitated the re-writing of many chapters, such as those, for instance, dealing with the alkaloids prepared from the tobacco plant, but the general method and plan of Prof. Pictet's work are preserved as closely as possible. The first part of the book deals with the artificial bases closely related to the natural alkaloids, pyridine and its homologues and derivatives, and the preparation and properties of them are described as fully as is necessary for the purpose. In the second part the natural alkaloids are classified, and their methods of synthesis discussed at length.

Die Riechstoffe. ("Aromatic Substances"). By DR. GEORG COHN. Braunschweig: Friedrich Vieweg und Sohn. 1904.

This treatise on the chemistry of aromatic substances forms a part of Bolley and Engler's "Handbuch der Chemischen Technologie," and deals very exhaustively with a subject which is full of interest both from a scientific and technological point of view. The chief desiderata in a work of this kind are accuracy and systematic arrangement, and in both of these particulars, as far as they can be tested, there seems to be no fault to find with it. The plants which yield ethereal oils are tabulated in families, and the physical constants and chemical constituents of

the oils are also conveniently given in tabular form. Great attention is paid to the isolation and synthesis of the aromatic substances, which are described in detail under the headings of the various classes of chemical compounds to which they severally belong. The quantitative determination of the oils is adequately treated, and the chapters on their physical and physiological behaviour, where the author finds more scope, are very interesting reading.

CORRESPONDENCE.

WILLIAMSON'S THEORY OF ETHERIFICATION.

To the Editor of the Chemical News.

SIR,—The following extract from Brande's "Manual of Chemistry," 1848, vol. ii., p. 1677, speaks for itself (it seems to me to contain Williamson's theory of etherification in a nutshell):—"The continuous supply of alcohol furnishes materials for the constant formation of sulphovinic acid, and the sulphovinic acid (containing 2 atoms of anhydrous sulphuric acid and 1 of alcohol) is no sooner formed than it is resolved into sulphuric acid, ether, and water . . ." The clause in the quotation within parentheses apparently simply means that Brande regarded sulphovinic acid as an acid sulphate. It looks from this that Williamson simply elaborated Brande's idea.—I am, &c.,

JOHN GEDDES MCINTOSH.

Analytical Laboratory,
9, Parsonage Street, Cubitt Town, E.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 25, June 20, 1904.

A New Carbide of Molybdenum, MoC.—H. Moissan and K. Hoffmann.—When a mixture of molybdenum, carbon, and excess of aluminium is heated in the electric furnace, a molybdenum carbide of formula MoC is formed. This is a hard substance, unattacked except with great difficulty by all acids but nitric. It is not decomposed by cold water or by water vapour at 600°. This carbide is analogous to Williams's tungsten carbide; this fact not being surprising, as molybdenum and tungsten are similar metals. It is also apparent that this compound enters into molybdenum steels under the form of double carbide. During its preparation it is observed that, at the boiling temperature of aluminium, a compound of molybdenum is formed which contains twice as much carbon as if its carburation took place at the higher temperature of the electric furnace.

Investigations on the Cementation of Carbon Steels and other Varieties of Steels.—Léon Guillet.—The author's researches show—(1) That the nitrogen in the cementation vessel has an action in certain cements by the formation of a cyanide; also cements containing potassium salts have a non-constant penetration velocity. (2) Elements merely dissolved in iron retard cementation, whilst those which are found to be in the state of a double carbide assist cementation. (3) Iron dissolves carbon considerably, even at moderate temperatures.

Formation of Isomorphous Mixtures of Lime and Lithia.—P. Lebeau.—By the fusion of a mixture of calcium carbonate and lithium carbonate in a current of carbon dioxide, a limpid product results, solidifying to a white crystalline mass. On digesting with a small quantity of

Preparation of Alkyl Sulphinic Acids.—Arthur Rosenheim and Ludwig Singer.—If dry sulphur dioxide is led into an ethereal solution of an alkyl magnesium haloid compound, the gas is absorbed with such evolution of heat

that external cooling of the vessel is necessary. After saturation a white crystalline mass is obtained, which may be re-crystallised from water, and is the pure magnesium salt of the sulphinic acid. This method is analogous to Grignard's for the preparation of monocarboxylic acids, by passing carbon dioxide into alkyl magnesium haloids.

Use of Sodium Peroxide for the Qualitative Analysis of Organic Substances.—Hans H. Pringsheim.

—The author describes a method for the qualitative determination of chlorine, bromine, iodine, phosphorus, arsenic, and sulphur by means of sodium peroxide. For this method he claims the following amongst other advantages:—It is absolutely trustworthy, the same product of ignition can be used for all six elements, the halogens if present together can be rapidly detected, and the method can be applied to volatile substances. Only a very small quantity of the substance is required, and the ignition is accomplished within one minute. The method is as follows:—To a weighed quantity of sodium peroxide 25 times its weight of a substance which contains much carbon and oxygen, and is not hygroscopic, is added, e.g., cinnamic acid or naphthalene. This mixture may be kept in a well-closed vessel. Enough of this oxidation mixture to cover the point of a knife is added to some grains of the solid or a few drops of the liquid in an iron tube, which is heated in a Bunsen burner till the beginning of the reaction is indicated by a decided odour. The tube is then cooled, the product of the reaction is dissolved in water, and the solution divided into two parts. The halogens and phosphorus may be detected in the usual way in the one after acidulation with nitric acid, and the sulphur and arsenic in the other after addition of hydrochloric acid. If bromine and iodine are present as well as chlorine, these elements can be conveniently separated in the solution made feebly acid with nitric acid on addition of chlorine water, and shaking with carbon disulphide.

Researches in the Camphor Group.—J. W. Brühl.

—The author describes the synthesis and properties of some halogen derivatives of camphor, especially di-iodocamphor and iodo-formyl-camphor. Claisen has shown that bromine with an alkaline solution of oxy-methylene camphor gives *o*-bromocamphor, while in an indifferent medium, such as perchloromethane, bromo-formyl-camphor is formed. The author now finds that iodine with an alkaline solution of oxy-methylene camphor always gives *o*-*o*-di-iodocamphor, and in absence of excess of alkali iodo-formyl-camphor may be isolated. This difference in the behaviour of iodine and bromine towards an alkaline solution of oxy-methylene camphor is all the more remarkable because the dibromo-compound is very stable, while the di-iodo body is far less so. Also of the two compounds which may be isolated in neutral solution the bromo-formyl-camphor is far more stable than the iodo-formyl camphor. It seems, however, that this latter, though actually the less stable, is more stable towards alkalis.

Determination of Palladium and its Separation from other Metals by means of Hydrazine.—P. Jannasch and W. Bettges.

—A weighed quantity of the previously purified metal is dissolved in about 5 c.c. of aqua regia, warmed for a short time on the water-bath, covered, and allowed to stand for some minutes. It is then heated more strongly, and finally evaporated to dryness. The residue is taken up with a little water to which about 20 drops of dilute hydrochloric acid have been added. It readily dissolves on warming on the water-bath, and the solution is then made up to about 120 c.c. To determine the metal, the faintly acid solution is heated almost to boiling, and the palladium is precipitated with 1 gm. of hydrazine sulphate (dissolved in about 20 c.c. of water). The metal begins to separate out at once with energetic evolution of nitrogen, and after warming for twenty minutes the reaction is complete. The fine black precipitate first obtained collects to form a spongy mass, which is washed and dried at 120° to 130° in a weighed asbestos ignition tube, and then reduced in a current of hydrogen. The

palladium thus obtained is a dull silver grey mass, and the author suggests that the black palladium which, according to the text-books, is separated from palladium solutions by means of zinc, iron, hydrogen, &c., consists really of a mixture of oxides. The precipitation of palladium in acid solution by means of hydrazine may be used to separate the metal from potassium, sodium, magnesium, zinc, and iron.

Separation of Mercury from Molybdenum and Tungsten by means of Hydrazine.—P. Jannasch and W. Bettges.

—*Separation of Mercury and Molybdenum.*—0.2 to 0.3 gm. of finely powdered molybdic acid is dissolved in water to which excess of ammonia containing a few drops of soda solution has been added. The solution is warmed on the water-bath to drive off excess of ammonia, and 2 to 3 grms. of tartaric or citric acid are added. Then mercury chloride is added, any turbidity being dissolved by means of a few drops of hydrochloric acid, and the solution is diluted to 100 c.c. It is then warmed to about 80° with addition of a warm solution of 2 grms. of hydrazine sulphate in 30 to 45 c.c. of concentrated ammonia. After heating for a quarter of an hour with frequent stirring it is allowed to stand for three or four hours, and then filtered. The precipitate of mercury is separated off, converted into sulphide, and determined as such, while the molybdenum in the filtrate is determined as tri-sulphide by the addition of ammonium sulphide, according to a method previously described by Jannasch. *Separation of Mercury and Tungsten.*—No tartaric or citric acid is added, but otherwise the method is essentially the same as the above. Ten to 15 c.c. of fuming nitric acid are added to the filtrate, which is then evaporated to 50 c.c., when tungstic acid separates out as a fine yellow precipitate, which may be dried and weighed. *Direct Determination of Tungsten in Tungstates.*—0.5 gm. of sodium tungstate is dissolved in 50 c.c. of water, and to the boiling solution is added a solution of 2 grms. of hydrazine hydrochloride in 10 c.c. of water and 20 c.c. of concentrated hydrochloric acid. A precipitate forms, and characteristic colour changes ensue. The precipitate, which becomes finally green coloured, is washed with very dilute nitric acid, dried, and ignited, and weighed as WO₃.

2-Phenyl-hypoxanthine and 2-Phenyl-adenine.—Wilhelm Traube and Ludwig Hermann.—2.3 grms. of sodium are dissolved in absolute alcohol, and 11.5 grms. of cyanacetic ester and 12 grms. of free benzamidine are added. After standing for twelve hours the liquid is quickly evaporated on the water-bath, the residue dissolved in water (a few drops of caustic soda being added if necessary), and acetic acid added till the solution is decidedly acid. 2-Phenyl-4-amino-6-oxypyrimidine collects in small colourless or yellow crystals, readily re-crystallised from hot water or alcohol. This is dissolved in dilute alkali and sodium nitrite, and dilute sulphuric acid gradually dropped in, the liquid being kept in constant motion. The iso-nitroso body is thus formed, and may be reduced by means of ammonium sulphide solution to 2-phenyl-4,5-di-amino-6-oxypyrimidine, which gives 2-phenyl-hypoxanthine with excess of concentrated formic acid. Freshly distilled phosphorus oxy-chloride converts the 2-phenyl-hypoxanthine into 2-phenyl-6-chlor-purine, which yields 2-phenyl-adenine when heated with saturated solution of ammonia under pressure for some hours.

Conversion of Sorbic Acid into Amino Acids.—

Emil Fischer and Fritz Schlotterbeck.—It is difficult to prepare diamino acids, especially those in which the amino groups are in the positions 1-3 or 1-4. The authors found that by heating sorbic acid with a large excess of concentrated aqueous ammonia for some time to 150° they obtained a body which possessed the properties of diamino acids and had the composition C₆H₁₄N₂O₂. It is thus a diamino caproic acid, but differs from the α - δ compound already known (inactive lysine). If the syrupy liquid is heated longer to 150° or distilled under greatly diminished pressure, it is partially converted into a crystalline product,

$\text{C}_6\text{H}_9\text{NO}$, which is the anhydride of an unsaturated amino-acid, $\text{C}_6\text{H}_{11}\text{NO}_2$, a derivative of normal caproic acid which we called amino-hexene acid. In all probability this compound is an unsaturated derivative of a methylated piperidone or pyrrolidone. Hence, in the original diamino caproic acid one amino group was in the γ or δ position to the carboxyl. Nothing definite can be said about the second amino group. The anhydride, when heated for some hours with excess of baryta water, forms an amino acid which, from its similarity to pyrrolidine carboxylic acid, may perhaps be methyl pyrrolidine carboxylic acid, which would easily be formed from δ -amino hexene acid.

MISCELLANEOUS.

Institute of Chemistry of Great Britain and Ireland.

—*Examination in Biological Chemistry. October, 1904.*—An Examination in Biological Chemistry will be held at the Laboratories of the Institute, commencing Tuesday, October 25th, 1904. The Examination will be open to candidates whose applications for admission to the Final Examination have been accepted by the Council, to candidates who have passed the Intermediate Examination, and also to Fellows and Associates of the Institute who desire to obtain a certificate of competency in this branch of work. The Examination will extend over four days, and may be theoretical, practical, written, and oral. The syllabus will include Biological Chemistry, with special reference to the Chemistry and Bacteriology of Foods, Water, Sewage, and Effluents, and to the practical applications of Biological Chemistry to Industries. Candidates intending to enter for the Examination are recommended to study the following subjects:—1. Elementary Biology. 2. The Morphology, Physiology, and Life History of Bacteria, Yeasts, and Moulds, in their relation to Food, Water Supply, the Treatment of Sewage, Agriculture, and the Fermentation Industries. (A special study of pathogenic organisms is not demanded, but the candidate should acquire a knowledge of such as are of importance in relation to Food and to Water Supply). Practical work should include:—(a) General bacteriological methods and preparation of pure cultures; (b) Microscopy: the staining and mounting of preparations, and the recognition of species; (c) Fermentation changes caused by micro-organisms. 3. Enzymes and their actions. 4. The methods employed in the examination and estimation of the carbohydrates. 5. The proteids and their decomposition products.

The Boiling and Evaporation of Metals in a Cathodic Vacuum.—F. Krafft.—The author has used distilling apparatus for his experiments made of fused blown quartz. Such apparatus supports a temperature of 1400° , and resists sudden changes of temperature perfectly well. He heats these tubes in an electric furnace, and measures the temperature by means of a thermoelectric junction. He has observed that in a cathodic vacuum fused metals emit vapours at relatively low temperatures, and he has succeeded in distilling a large number. Zinc gives off vapours at as low a temperature as 300° , and distils at about 640° ; cadmium distils at 450° , selenium at 380° , tellurium at about 550° , lead at 1180° ; tin does not vapourise at 1100° ; antimony distils at 775 – 780° , bismuth at about 1045 – 1050° ; silver sublimates rapidly at 1200° without distilling, copper sublimates at 1315° , its boiling-point is probably about 1500 – 1600° ; gold sublimates slowly at 1375° . Finally, the author has observed that the boiling-point rises when the height of the column of vapour of the metal formed above the surface of the boiling liquid increases. He considers that boiling in vacuum consists first of the formation of vapours which thus produce an atmosphere, and that boiling takes place when the vapour tension of the liquid is equal to the pressure which exists on the surface. Thus we understand why the boiling-point rises when the column of vapour increases in height.—*Berichte*, vol. xxxvi., p. 1690.

The Sanitary Institute.—The Twenty-second Congress of this Institute will be held at Glasgow from July 25th to 30th, under the Presidency of the Right Honourable Lord Blythswood, LL.D., Lord-Lieutenant of Renfrewshire. A lecture will be given to the Congress on July 27th by Sir Richard Douglas Powell, Bart., M.D., &c., on "Prevention of Consumption," and a number of Popular Lectures will be given during the week in the Exhibition which will be held in connection with the Congress. There will be three Sections as follows:—Section I. Sanitary Science and Preventive Medicine—President, Prof. J. Glaister, on July 26th and 27th. Section II. Engineering and Architecture—President, Prof. Henry Robinson, M.Inst.C.E., on July 27th and 28th. Section III. Physics, Chemistry, and Biology—President, Prof. Frank Clowes, D.Sc., &c., on July 28th and 29th. Conferences on various subjects connected with Sanitary Science will also be held, and numerous papers will be read and discussed. On Saturday, July 30th, excursions will be made to various places of interest in the neighbourhood; also during the week there will be several entertainments, such as Garden Parties, Concerts, Receptions, and Afternoon and Evening Cruises. Further information can be obtained from the local Secretary, Mr. J. Lindsay, City Chambers, Glasgow, or E. White Wallis, Esq., the Secretary of the Institute, Margaret Street, London.

Solubility of the Red and Yellow Oxides of Mercury and their Dissociation.—Karl Schick.—The question of the identity or the isomerism of the red oxide and the yellow oxide of mercury has been already the subject of several papers. The author agrees with the opinion expressed by Ostwald, according to which the two bodies are identical chemically, but differ in the size of their particles; relying on this opinion, he has measured their solubility in distilled water at a temperature of 25° . By operating with carefully purified water, and of which the purity was controlled by measurements of conductivity, and taking care to prolong the experiment sufficiently to make certain of reaching a state of equilibrium, he found the following results:—The solubility of the yellow oxide was 0.0518 grm. per litre, or 1 part of oxide in 19,300 parts of water; the solubility of the red oxide was 0.0513 grm. per litre, or 1 part in 19,500 parts of water; thus the two solubilities were practically equal. Ostwald's opinion is again confirmed by the fact that during the measurements made on the red oxide, the author has observed the transformation of this body into the yellow oxide. Measurements made in boiling water, for a few hours only, have given the following results:—For the yellow oxide, 0.41 grm. per litre, or 1 part in 2400 parts of water; for the red oxide, 0.38 grm. per litre, or 1 part in 2600 parts of water. It cannot be doubted but that more prolonged experiments would give still closer solubilities. The presence of the ions OH , increases the solubility of the oxide of mercury in water, proportionally to their quantity. This may be explained by the fact that these dissolved metallic oxides (alkalis or alkaline earths), when in contact with solutions of mercuric oxide, give salts in which the mercury forms a complex anion with the oxygen. Solutions of mercuric oxide are the seat of a very slight dissociation, as is shown by the measurements of saponification and conductivity; their prolonged contact does not perceptibly saponify acetate of ethyl at 25° , but the addition of a neutral salt causes a rapid saponification; their conductivity is very slightly better than that of the water employed to make them. The addition of haloid salts to these solutions increases their proportion of ions of OH , on account of the formation of sublimate or of complex mercurio-haloid compounds. The reaction is relatively slow, but its speed can be increased by the addition of a large excess of an alkaline haloid, so that it becomes practically instantaneous and complete. Finally, it has been observed that the colour of the yellow oxide depends on the temperature, and that when this rises the colour passes progressively from yellow to red.—*Zeit. Physik. Chem.*, vol. xlii., p. 155.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

Founded 1877. Incorporated by Royal Charter 1885.

An EXAMINATION IN BIOLOGICAL CHEMISTRY, with special reference to the Chemistry and Bacteriology of Foods, Water, Sewage, and Effluents, and to the practical applications of Biological Chemistry to Industries, will be held at the Laboratories of the Institute, commencing on **TUESDAY, the 25th day of OCTOBER, 1904**, and will extend over four days.

The Examination will be open to Candidates whose applications for admission to the Final Examination have been accepted by the Council, to Candidates who have passed the Intermediate Examination, and also to Fellows and Associates of the Institute who desire to obtain a certificate of competency in this branch of work.

The List of Candidates will be closed on **TUESDAY, the 26th day of SEPTEMBER, 1904**. For further particulars apply to the REGISTRAR, 30, Bloomsbury Square, London, W.C.

"The Book of Regulations" for Admission to the Institute can be obtained from Messrs. Blundell, Taylor, & Co., 173, Upper Thames Street, London, E.C., price One Shilling.

THE DAVY FARADAY RESEARCH LABORATORY OF THE ROYAL INSTITUTION.

Directors:

The Right Hon. LORD RAYLEIGH, O.M., M.A., D.C.L., LL.D., Sc.D., F.R.S.

SIR JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

Superintendent of the Laboratory:

DR. ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

This Laboratory was founded by DR. LUDWIG MUND, F.R.S., as a Memorial of Davy and Faraday, for the purpose of promoting, by original research, the development and extension of Chemical and Physical Science.

MICHAELMAS TERM.—Monday, October 3, to Saturday, December 17.

LENT TERM.—Monday, January 9, to Saturday, April 15.

EASTER TERM.—Monday, May 8, to Saturday, July 22.

Full information and forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

To prevent delay Candidates ought to send in their applications for admission during the course of the Term preceding that in which they wish to enter.

BIRKBECK COLLEGE

(BIRKBECK INSTITUTION),

Breams Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS ..	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING ..	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board, Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.

ST. PAUL'S SCHOOL, West Kensington.—

An EXAMINATION will be held at the above School on Tuesday, September 6th, 1904, and on the following days, for filling up about Twenty Vacancies on the Foundation.—Full particulars of the Examination can be obtained on application to the Bursar.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC, As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, SHOT, &c.

UNIVERSITY OF BIRMINGHAM.

Faculties.—

**SCIENCE.
ARTS.**

**MEDICINE.
COMMERCE.**

SPECIAL SCHOOL OF MODERN LANGUAGES.

DEPARTMENT FOR TRAINING OF TEACHERS.

Schools of—

**ENGINEERING,
METALLURGY.**

**MINING,
BREWING.**

DENTISTRY.

Leading to Degrees and Diplomas.

The Session 1904-5 commences October 3rd, 1904.

ALL COURSES AND DEGREES ARE OPEN TO BOTH MEN AND WOMEN STUDENTS.

In the Medical School there is a separate Dissecting Room for Women, with a qualified Woman Demonstrator.

Graduates of other Universities may, after two years' study or research, take a Master's degree.

SYLLABUSES with all information will be sent on application to the Secretary.

THE DURHAM COLLEGE OF SCIENCE, NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided

for Students of both sexes proceeding to the University Degrees in Science, or in Letters, and for the University Diploma in Theory and Practice of Teaching. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 26th.

Lectures begin October 4th, 1904.

Prospectuses on application to the SECRETARY.

INSTRUCTION IN PURE CULTIVATION OF YEAST. According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeast brewers', distillers', wine, disease yeasts, moulds, and bacteria.

Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jørgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufactories, &c.

Further particulars on application to the Director—

ALFRED JØRGENSEN, The Laboratory, Copenhagen, V.

ABSOLUTE ALCOHOL, FREE FROM DUTY, FOR SCIENTIFIC AND RESEARCH WORK IN LABORATORIES.

To be obtained from

HUGO LORENZ,
7-8, Idol Lane, Great Tower St., London, E.C.,

Licensed Trader in Alcohol and Spirits of Wine.

Stock kept in suitable packages ready for immediate use.

Young German Chemist (Dr. Phil. Nat.;
highest degree Heidelberg Univ., "Summa cum laude") wants
Situation in Works or Laboratory. Best references.—Address, S.,
184a, Ladbroke Grove, W.

SHELLAC PATENT, No. 4550.

LICENSE FOR ENGLAND, eventually
also for the UNITED STATES OF AMERICA, Patent
No. 760547, FOR SALE. High profit. Approved proceeding for
Varnishes, Polish, Hat Manufacture, Sealing-wax, Finishes, &c.

For particulars apply to CARL CORDES, MAGDEBURG, GER-
MANY.

THE CHEMICAL NEWS.

VOL. XC., No. 2331.

THE ATOMIC WEIGHT OF TUNGSTEN.*

By EDGAR F. SMITH and FRANZ F. EXNER.

(Continued from p. 39).

TAYLOR's experience re-emphasised the absolute necessity of satisfying ourselves beyond every reasonable doubt that the material for the atomic weight determinations was pure; at least as pure as the means at hand would furnish. The admission of Schneider that his purest substance contained traces of impurity, insoluble in caustic potash, and Taylor's discovery that every sample of tungsten trioxide tested by him gave a residue, insoluble in sodium carbonate, made us very solicitous regarding the purity of all material which had been used in any previous investigations, for it will be found upon consulting the literature that almost every experimenter was content to proceed with ammonium paratungstate which was perfectly white in colour. Three to five re-crystallisations were held to be sufficient to attain that condition.

Our doubts became so overwhelming that it was decided to begin the work anew with the mineral wolframite, and to ascertain, once for all, what it contained in order that search might be made for all such constituents, and every effort put forth to ensure their perfect removal from the salts which might be experimented upon. Accordingly, in the summer of 1901 large quantities of wolframite, from Lawrence County, S.D., were decomposed, and the resulting tungstic acid converted into ammonium paratungstate. The mother-liquors from the salt were black in colour, and gave in due time the interesting compound—ammonium vanadico-phosphotungstate—described by us in the *Journ. Am. Chem. Soc.*, xiv., 573. Its discovery added, of course, vanadium and phosphorus to the list of possible contaminating substances: columbic oxide, silica, molybdic oxide, ferric oxide, manganese oxide, &c. Large amounts of ammonium paratungstate were taken for the purification of the tungsten trioxide by methods which may now be presented.

Method 1.—This first fraction was collected apart, dissolved in distilled water, and re-crystallised; the first crystallisation was again set aside and dissolved, this operation being repeated ten times. A portion of the sixth crystallisation was ignited in a platinum crucible, and the resulting oxide was digested on a water-bath with a 2 per cent solution of sodium carbonate free from iron. The oxide dissolved, but its solution was quite turbid. Upon standing, a white residue settled out, which after washing with water and decomposition with a few drops of hydrochloric acid, showed tungstic acid and iron. Portions of the tenth re-crystallisation behaved similarly. The mother-liquors, including that from the tenth crystallisation, assumed a dark brown colouration upon concentration, indicating thereby that not only iron, but that also the vanadico-phosphotungstate, already alluded to, continued with the ammonium tungstate. Vanadium too was found in a portion of the tenth crystallisation when it was heated in an atmosphere of hydrochloric acid gas. Hence it was concluded that this method was unsatisfactory, and it was abandoned. Chemists, who in the past were content to look upon ammonium paratungstate as being very pure when its colour was perfectly white (and from published statements most have been content with this criterion), which it is after the third or fourth crystallisation, cannot have had pure substance for their investigations, hence the fluctuation in their results is easily comprehended.

Method 2. This may be called the method of Borch. In it the mineral was fused with sodium carbonate, the fusion exhausted with water, and after filtration the liquid was precipitated with calcium chloride. The resulting calcium tungstate was filtered, washed, and decomposed with hydrochloric acid. The liberated tungstic acid was dissolved in ammonia water, and the ammonium salt crystallised out. The method was carried out with rigid adherence to the printed instructions, but it proved entirely unsatisfactory.

Method 3.—Solutions of ammonium paratungstate, decidedly brown in colour, were boiled with precipitated calcium carbonate. Ammonia and carbon dioxide were evolved, while calcium tungstate was precipitated. The solutions lost nothing in colour. After filtering out and washing the calcium tungstate it was boiled with hydrochloric acid. Tungstic acid of a rich yellow colour separated. It was washed and dissolved in ammonia water. There was a very slight bluish coloured residue. The ammonium paratungstate, which crystallised out, was perfectly white in colour, but a portion of it ignited, and the resulting oxide, digested with a dilute sodium carbonate solution, disclosed the usual white residue in which tungsten and iron were found.

The salt, purified in this way, was fully as free from impurities as a salt which had passed through six crystallisations from water. This fact led us to prepare pure calcium carbonate and hydrochloric acid before repeating the method with another portion of ammonium paratungstate.

Commercial calcium carbonate was boiled with a solution of pure ammonium chloride. Iron and other impurities remained with the excess of calcium carbonate. The filtrate from the latter was precipitated with pure ammonium carbonate. The resulting calcium carbonate was thoroughly washed, and then dried.

Ordinary hydrochloric acid was saturated with calcium chloride, and after the addition of phosphorus pentoxide was distilled with water. This gave pure acid. With these purified reagents ammonium paratungstate, which had passed through several crystallisations, was subjected to the treatment outlined in the beginning of this section. The purified salt, when tested, showed but traces of impurities, and it is very probable that these, after several repetitions, would disappear entirely. The actual trial was not made, because another course seemed to lead to the desired end in a much shorter period. Experience also showed that nitric acid was preferable.

Method 4.—In this procedure a boiling solution of ammonium paratungstate was decomposed with hydrochloric acid. The precipitated tungstic acid was again dissolved in ammonia, and the decomposition repeated. Repeating this process several times yielded tungstic acid which might be asserted to be quite pure, although when the mother-liquors from the several fractions of the ammonium salts were reduced to a small volume the dark colour appeared. A white residue, although slight, was also obtained from the ignited tungsten trioxide. Wyman (Thesis, University of Pennsylvania, 1902) found, after twenty-five decompositions with hydrochloric acid, evidences of similar contamination. This chemist tried seven different schemes in his endeavour to obtain pure tungstic acid, without the desired result. Accordingly, on resuming this part of our study in the summer of 1902 we determined to eliminate every possible source of contamination from the various reagents which we proposed using. Thus, 15 litres of hydrochloric acid were purified as already described. It was free from every impurity, which was proved by carefully repeated tests. Eighteen litres of nitric acid were distilled after the addition of pieces of pumice and some sodium hydrogen phosphate. The product left no ponderable residue when a definite volume of it was evaporated to dryness in a platinum vessel. The sodium carbonate was made pure by fusing it in a platinum vessel, and introducing into the molten mass a small quantity of pure, precipitated calcium carbonate which dissolved, the mass

* From *Proceedings of the American Philosophical Society*, vol. xliii., No. 176.

being held for five minutes in the liquid state. After cooling, the fusion was allowed to dissolve out in cold water. The calcium carbonate, iron, &c., were filtered off, and the solution evaporated to crystallisation. The sodium carbonate which separated was re-crystallised four times. Platinum vessels were used for the purpose. They are essential. Portions of the purified salt were examined for silica and iron, and their absence demonstrated. There was now every reason to believe that the reagents, including the water (for it had been re-distilled), were pure. They contained nothing which would contaminate the tungsten trioxide. Therefore if the latter left a residue upon digestion with a dilute sodium carbonate solution, that residue plainly came out from the tungstic oxide.

And now we must digress a little. Wyman experienced difficulty and annoyance in his efforts to dissolve tungstic acid in ammonia water. Others have had, doubtless, similar experiences. There invariably remains a bluish-white mass which no amount of ammonia or protracted boiling eliminates. More than a kilogram of this substance had accumulated from Wyman's work, and came into our possession. Its bluish-green tint suggested the presence in it of some reduction product, probably occasioned by the hydrochloric acid. We accordingly projected the mass into boiling concentrated nitric acid. A violent evolution of chlorine immediately followed, and continued until the material had acquired a rich yellow colour. Whence came the chlorine? More of the blue residue was dried at 100°, then heated upon a platinum-foil. Great volumes of ammonium chloride were expelled, leaving pale yellow coloured tungsten trioxide. An analysis of a portion of the dry, bluish material was made, when 5.48 per cent of NH_4 and 9.65 per cent of Cl were found. The presence of this amount of foreign substance could only be accounted for on the assumption that in the liberation of tungstic acid from ammoniacal solutions of ammonium tungstate with hydrochloric acid portions of the latter and of the ammonium chloride were so combined that no amount of washing would remove them. They are retained, and firmly, by the tungstic acid. Let those who question this examine the white, slimy residue which appears on attempting the solution of tungstic acid in ammonia. Most of us have quieted our consciences on this point by asserting that such residues are those "persistently insoluble paratungstates." If the solution from such residues be re-precipitated with hydrochloric acid, quantities of insoluble bodies again appear. These are beyond question ammonium chlorinated tungstic acid derivatives, which even prolonged boiling with concentrated acids will not change to the yellow acid. They merit further study.

The preceding experience emphasised the necessity of removing all the ammonium chloride in tungstic acid if the precipitation method of purification was to be pursued. This was done in the following way:—Two to 3 litres of concentrated nitric acid, diluted with water to half their volume, were heated in a large porcelain dish until it began to fume strongly, when 25 c.c. of pure hydrochloric acid and 3 kilograms of dry and fairly pure ammonium tungstate were added. Vigorous action set in, and volumes of decomposition gases escaped. The mixture was constantly stirred during the operation. As soon as the action diminished, 10 to 15 c.c. of pure hydrochloric acid were introduced at intervals. As the decomposition approached completion, the yellow tungstic acid lost its porous character, and collected as a heavy granular powder upon the bottom of the dish, but it was heated with occasional stirring for a period of from three to four hours. At the expiration of that time, there remained only tungstic acid, and nitric acid with traces of chlorine and ammonia. The tungstic acid was washed by decantation with pure distilled water until the tungstic acid suspended in the solution subsided very slowly, and the wash-water from it showed but a faint acid reaction. The subsided yellow-coloured acid was placed in a porcelain dish, hot distilled water was poured over it, and ammonia was conducted into the solution. As a rule, all of the acid dissolved, and there was at

the most a very small residue. Thus 45 litres of a saturated solution contained a residue which weighed less than 2 grms.

The ammonium paratungstate separating from such a solution showed the needles and plates characteristic of that salt. Only the first three fractions were preserved. They represented seven-eighths of the entire substance. The other portions were set aside. A second and a third treatment, as outlined above, was given the first three fractions, and when the salt, finally obtained, was subjected to the sodium carbonate test, allowing the solution to stand over-night, it remained absolutely clear. The mother-liquor from the salt, reduced to 5 c.c., remained colourless. One object in this long and baffling study had at last been obtained. We were the possessors of 700 grms. of pure ammonium paratungstate.

Three kilograms of impure ammonium paratungstate were decomposed by acids as described above, the operation being repeated five times, when the ammonium salt from the last decomposition responded admirably to the crucial tests. This salt disclosed none of the substances which were found accompanying the tungstic acid originally, hence the latter was considered pure, and was applied as will appear in subsequent paragraphs. However, before proceeding further it seems proper to direct attention to certain other experiences which possess interest and value.

The Residue obtained by Digesting Tungsten Trioxide with Sodium Carbonate.

Ammonium paratungstate, after three crystallisations, and when quite white in colour, was ignited in a platinum crucible. Two hundred grms. of oxide were obtained in this way, and were digested with a 2 per cent solution of sodium carbonate of excellent commercial quality. Quite a residue appeared. It was washed and dried. A portion, weighing 0.4712 gm., was digested with aqua regia. The insoluble part weighed 0.4309 gm., while the solution of the soluble constituents, weighing 0.0403 gm., was reduced to a small volume, diluted with water, and precipitated with ammonia. The iron weighed 0.0337 gm. as ferric oxide. Manganese and platinum were also found. The tungsten trioxide, when digested with hydrofluoric acid, lost 0.0149 gm., representing silica. Or, if the results be tabulated, they show:—

	Grm.	Per cent.
Weight of residue	0.4712	—
" WO_3	0.4160	88.28
" SiO_2	0.0149	3.16
" Fe_2O_3	0.0337	7.15
Manganese, platinum, &c. Undet.	—	—

98.59

Even pure sodium carbonate will not remove all of the impurities, although it may serve to test the purity of the oxide as to the iron, &c., which may be present.

Ignition of Ammonium Paratungstate.

The ignition of this salt in platinum vessels, as ordinarily conducted, contaminates the trioxide with platinum. To minimise this contamination a platinum crucible was fitted tightly two-thirds of its length into an asbestos board. A platinum-wire shaped into a tripod was set upon the bottom of the crucible. A smaller platinum crucible was supported by the tripod. Into the latter were introduced from time to time not more than from 2 to 3 grms. of ammonium tungstate. A red heat was applied to the outer crucible. The ammonia was expelled in the course of half-an-hour, when the crucibles were covered with an inverted porcelain lid, it being lifted from time to time to admit air. Constant weight was obtained in two hours. This procedure gave the best results which could be gotten by the use of platinum crucibles. While the oxide is cooling it should be protected from all reducing atmospheric dust, because the hot oxide is extremely sensitive to the action of such substances. This is evident from the following:—A platinum-rod previously heated in a flame

and applied to the hot oxide produces no change, but if the rod be touched quickly to the skin and then laid on the hot oxide, a green spot will appear at the point of contact.

The efforts to substitute silver and gold crucibles for those of platinum demonstrated that these metals, too, were appreciably absorbed by the oxide. Porcelain crucibles were used, notwithstanding the absorption of silica, which would of course become greater as the time of ignition was prolonged and as the heat was increased. Further, the oxide in immediate contact with the porcelain invariably showed a green colour. The glaze of the crucible always indicated etching. With an unglazed crucible the action was not so evident, hence the contamination was not so great, and the most satisfactory results were gotten by setting the unglazed porcelain crucible in a platinum crucible and bringing about the ignition of the salt in this double-walled chamber. The colouration of the surface of the oxide was extremely slight. Experience, however, eventually showed that the best course to pursue consisted in digesting the ammonium paratungstate directly in a porcelain casserole with pure nitric acid and a few c.c. of hydrochloric acid until it was completely decomposed, and the ammonia and hydrochloric acid were destroyed. When the tungstic acid was evaporated to complete dryness, it showed a rich orange-yellow colour. It was transferred to an unglazed porcelain crucible, and there ignited gently for half-an-hour. This may be done over a direct flame, the crucible being covered with an inverted porcelain lid. Any enclosed nitric acid was expelled by the gentle heat, and the weight soon became constant. The resulting tungstic oxide had a uniform yellow colour. Green was absolutely absent. This procedure eliminated the reduction caused by the ammonia, and it may be added that by its use glazed crucibles were employed every day in similar ignitions for several weeks without showing the least etching or corrosion of the surface.

Having at last gotten pure salt and pure oxide, the question arose as to what method should be adopted in the determination of the atomic weight of the metal. The method proposed by Taylor (see *ante*) was new. The results he obtained were with material not especially purified, yet their fair agreement pointed to the possibility of arriving at a definite value with the pure substance, such as was now available. Preliminary trials were executed according to Taylor's suggestions, using glass apparatus just as he had done, and drying at 400° to constant weight. The weighings were all made on the same day and under uniform conditions. The main purpose was to ascertain whether concordance in results could be realised. The results in the subjoined table show the opposite:—

	Na ₂ CO ₃	WO ₃	CO ₂	Atom. weight.
	Grms.	Grms.	Grms.	
1.	5.9	2.45645	0.16775	183.07
2.	5.6	2.72292	0.51785	183.36
3.	5.5	3.32953	0.63288	183.48
4.	4.7	3.96720	0.75473	183.29
5.	4.0	3.44944	0.65489	183.75
6.	4.1	3.41273	0.64796	183.74
7.	4.8	6.10309	1.16087	183.32
8.	3.9	6.39735	1.21644	183.39
9.	3.5	2.17150	0.41332	183.40
10.	3.1	1.57903	0.29966	183.85

The trioxide used in Experiments 1 to 4, inclusive, was obtained by gently igniting the ammonium salt in a porcelain crucible. That used in Experiments 5 and 6 was strongly heated in a porcelain crucible. In 7 and 8 the ammonium tungstate was heated for one hour in a double platinum crucible. The oxide in Experiment 7 had been heated two hours in the same kind of crucible, while in Experiment 10 the ignition continued for two hours in the double platinum crucible. The gradual rise in the value to 183.85 by protracted heating could surely not be due to the expulsion of volatile matter, for there was no change in weight after the first hour of ignition in the double crucible. Evidently the oxide absorbed impurities which led to the

rise in the atomic weight. Accordingly, samples of ammonium paratungstate were ignited under conditions as nearly similar as possible in crucibles of platinum and of porcelain. The values from the oxide in the crucibles of porcelain were higher than those from the oxide made in platinum crucibles, showing in all probability that the oxide took up more foreign material from the porcelain than from the platinum. Therefore the mere ignition of the ammonium salt in vessels, such as have been described, drew in sources of error. These would, of course, have to be eliminated if the method was to be tested upon its own merits. It was sought to accomplish this by igniting thoroughly dry ammonium paratungstate, and ascertain the loss (water and ammonia) sustained by different amounts, which resulted in discovering that the percentage of volatile matter could be obtained to within less than 0.01 per cent, which would answer for the purpose of atomic weight determination. And therefore, in the actual experiments, the ammonium paratungstate was weighed out directly into the flask, it being only necessary to make the proper calculations to arrive at the amount of trioxide which was then used. Six determinations were made; the results in the atomic value varied from 183.4 to 183.81. The early explanation for the lack of concordance, if the method was not faulty, would be to suppose that the action of the soda upon the glass would withdraw varying amounts of silica, and there would follow, of course, the liberation of corresponding amounts of carbon dioxide. If this really occasioned the error, it was hoped that the substitution of a platinum bulb, similar to the glass vessel, would lead to success. This was done. The experiments were performed as before, with slight modifications where it was considered advisable and advantageous. The atomic values in a series of five trials ranged from 182.85 to 183.64. Patient search was made for the reason, every step being tested repeatedly, until eventually the conclusion was forced upon us that carbon dioxide, in varying amounts, was disengaged through the decomposition of the sodium carbonate in the final drying. Jacquelin (*Yahresb.*, 1860, p. 116; *Ann. Chem.*, [4], xxviii., 86; and *Ann. Chem.*, [3], xxxii., 205) showed that this salt loses from 0.03 to 0.05 per cent in weight at 400°, and other observers have shown that the loss continued with the length of the period of ignition and with the temperature. Here, then, was a serious defect in the method which would explain why the values found were low, and why they differed so widely. The attempts to correct this weak point proved futile, so that the method, having had a thorough trying-out, was abandoned after months of arduous work.

It was hoped that perhaps a normal silver tungstate might be made, which after solution in potassium cyanide could be electrolysed and the value of tungsten obtained from a comparison with the precipitated silver. Fifteen experiments were made. In one series (the best) of five experiments the results varied from 184.00 to 184.39. It was found, after much search, that there could be no certainty as to when a normal salt was really in hand. Washing and drying, even when performed with the utmost care, occasioned a change in the character of the salt. The method was discarded.

An effort was also made to obtain a cadmium salt of definite composition. Much time was given to it, and experiments were made in the electrolysis of bodies believed to be uniform in composition. The atomic values ranged from 181.90 to 185.71.

Having subjected three new methods to vigorous tests in our efforts to solve the problem along new lines, and having found them utterly deficient, the hope still remained that possibly some of the earlier methods might with pure material give satisfactory results. The writers felt, without meaning to reflect in the slightest upon earlier investigators, that their material possessed the merit of superior purity; and if that were really the case, older methods, simple in principle and easy of execution, might well be expected to give concordant values. Of the 175 experiments made by the entire corps of previous investigators, there is but one short

series, namely, that of Pennington and Smith, in which there is that degree of concordance which is desirable and necessary in fixing the atomic value of any element. Splendid as is the work of Schneider, worthy as it is of high praise, there still remains the fact, not to be pushed aside, that between the minimum and maximum values there is a difference of more than a unit. The atomic value given by Schneider, Hardin, and others for tungsten is 18.4—the mean of very widely differing series. Cognisant of these facts, with faith in the greater purity of our material, steps were taken to repeat several older procedures.

(To be continued).

THE CONSTITUTION OF THE AMMONIUM COMPOUNDS.*

By JOHN CANNELL CAIN, D.Sc., M.Sc.

(Concluded from p. 41).

THE constitution of the metal ammonium compounds is sufficiently indicated by the formulæ $H_3N = ClAg$, $H_3N = ClCu$, $H_3N = ClPtCl$, NH_3 for the compounds of ammonia with the chlorides of silver, copper, and platinum respectively.

The correctness of this theory is rendered the more probable by the ease with which it explains the existence of the isomeric quaternary ammonium salts, to which reference has already been made. The stereochemical configuration of ammonium chloride and its substitution products, according to the usual ammonium theory, presents a special difficulty, owing to the fact that no symmetrical solid geometrical figure with five corners exists. In order therefore to arrive at a space formula, it became necessary to assume that certain valencies attached to the nitrogen atom are arranged in special directions. This is obviously a very grave assumption, and one which, of course, has no parallel in the very simple configuration of the carbon atom. In this way has been developed the cubic formula of van't Hoff, the double tetrahedron of Willgerodt, and the square pyramid of Bischoff. If we, however, accept the formula which is here presented, no new assumption has to be made in order to arrive at a space configuration. The nucleus $N = Cl$, instead of a carbon atom, is supposed to be at the centre of a tetrahedron, and we have—



The number of possible isomers is shown by the accompanying table.

General formula.	No. of isomers.	Formulæ of isomers.
NAAAACl	1	$A_3N = ClA$.
NAAABCl	1	$A_3N = ClB$, $A_2BN = ClA$. (a)
NAABBCl	2	$A_2BN = ClB$, $AB_2N = ClA$.
NAABCCl	3	$ABCN = ClA$, $A_2BN = ClC$, $A_2CN = ClB$.
NABDCCl	4	$BCDN = ClA$, $ACDN = ClB$, $ABDN = ClC$, $ABCN = ClD$. (b)

(a) These would be the formulæ of Kipping's hyridramine salts (*loc. cit.*).

(b) Three of these have been prepared in the case of the phenyl methyl allyl benzyl ammonium iodides; two optically active (Pope and Peachey, *loc. cit.*) and one inactive (Wedekind, *loc. cit.*).

The corresponding formulæ for acids other than hydrochloric are easily written.

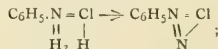
The formula for tetramethylammonium iodide, viz.,

$(CH_3)_3N = ICH_3$, also explains its reactions much better than does the usual one (compare Armstrong).

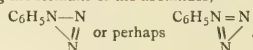
The fact that a comparatively small number of isomers indicated by the above formulæ exists, is to be expected, for the isomers would in many cases differ greatly in stability. There would be a "stable" and a "labile" form, and often the labile would pass into the stable form so quickly as to prevent its isolation.

The ammonium theory has been freely used in the past in order to arrive at a formula for analogously constituted bodies; thus we have the phosphonium, arsonium, stibonium, sulphonium, oxonium, and diazonium compounds. We should, in view of the new theory, write the general formulæ $H_3P = ClH$, $H_3As = ClH$, $H_3Sb = ClH$, $H_3S = ClH$, $H_2O = ClH$, corresponding to $H_3N = ClH$. The diazonium salts—which are now considered to be derived from, e.g., aniline hydrochloride, by the replacement of three hydrogen atoms by one nitrogen, thus $C_6H_5N.Cl \rightarrow C_6H_5N.Cl$

(a mode of representation which does not account for the explosive nature of these compounds)—would be better written, in my opinion, as follows:—

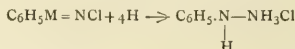


resembling the formulæ of the azoimides,—



This mode of representation of the diazonium salts resembles both the older formula of Kekulé and the later one of Blomstrand in several important respects.

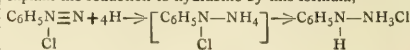
In Kekulé's formula, $C_6H_5.N = N.Cl$, the double linking between the nitrogen atoms shows a close analogy to the azo-compounds, and the position of the chlorine atom easily explains the formation of hydrazines, thus—



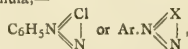
The Blomstrand formula, on the other hand,



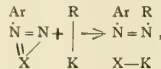
shows the presence of pentad nitrogen, and is analogous to the existing ammonium theory. It is difficult, however, to explain the reduction to hydrazine by this formula,—



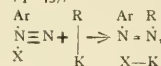
The new formula,—



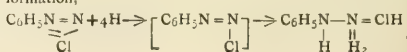
explains the transition of a diazonium salt into a syn-diazo compound, thus—



avoiding the change of linkage necessary according to Hantzsch (*loc. cit.*, p. 45),—

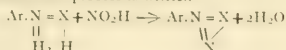


and provides an easy representation of the hydrazine formation,—

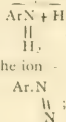


* From the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, 1904, xlviii., No. 14.

The diazotisation process is written—

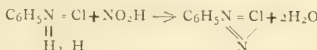


the complex ion,—

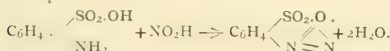


being transformed into the ion—

thus, in the case of aniline, we have—



and sulphanilic acid—



The other reactions of diazonium salts, as well as those of the phosphonium, arsonium, &c., compounds, are similarly written.

NOTES ON GRAVITY AND CHEMICAL ACTION.

By W. P. DREAPER, F.I.C., F.C.S.

SINCE the days of Newton and the discovery of the law of gravity, the nature of this force has always been a subject for speculation and theory.

"The reason of these properties of gravity I have not as yet been able to deduce, and I frame no hypothesis," said Newton; and again, "gravity must be caused by an agent acting constantly according to certain laws."

Speculation and experimental science have since been occupied in trying to discover the nature of this universal force. The names of Mohr, Du Bois Reymond, Huyghens, Secchi, Le Sage, and others are closely connected with this subject.

All modes of action seem to be propagated radially from a centre in progressive oscillations in an elastic media. It is natural, therefore, to look in some such direction for the physical cause of gravitation. But all the theories which run on these lines are open to the objection that gravity acts instantaneously. Le Sage's theory assumes, on the other hand, that all space is constantly traversed by streams of infinitely small particles moving in all directions and with extreme velocities. Any two bodies acting as screens to these particles will protect each other from a certain number of impacts. These bodies are consequently driven towards one another. Clerk Maxwell's objection to this theory seems to be fatal to its acceptance. If one, however, substitutes "lines of force" for "ultramundane particles" his objections perhaps have not the same force. With this modification it seems possible to explain Shellbach's experiments, since re-discovered by Prof. Guthrie, on the grounds that the vibrating disc interferes with these lines of force. The latest idea of Prof. J. J. Thomson, that these lines are not imaginary but actually exist, also supports this view. It is perhaps unnecessary to draw attention to the other theories which have from time to time been brought forward. They have not received much support from modern thinkers.

In bringing forward the following theory I derive a certain amount of support from the fact that there is some evidence that Newton himself regarded gravity as a secondary phenomenon. Of such a nature is my theory.

Gravity in the past seems to have been regarded as a direct force, only differing from electrical or light phenomena in the fact that it acts instantaneously. All other

forces that we know of take a measurable time to traverse the ether space. The idea is here put forward that gravity is not a direct force in this sense of the word. This overcomes the difficulty of bringing such a constantly acting force into agreement with the theory of the conservation of energy.

The proposed theory stated in terms is as follows:— Gravitation is the result of the sum of all the forces, here collected under the term energy, passing or desiring to pass from one body to another through a resisting medium. This can be translated into a direct pull. The object of this transfer is to establish an equilibrium of force in space. This probably means the physical death of matter, the breaking down of the atom into its ultimate state, the establishment of a universal condition of rest. It is unnecessary, however, to assume that this condition will ever be reached, as explained further on.

We have recently obtained some idea of the energy stored up in the radium unit, and the result expressed in ordinary standards is immense. We also know that there is a gradual "leakage" leading to the breaking down of the complex-unit. These well-known facts are simply noticed, in passing, as showing the relation of this theory to the "New Chemistry." According to this new theory, the tendency to reduce the intervening space between two bodies, in order that this may take place more readily, is what we call gravity.

It is perhaps necessary from this view to regard all energy as kinetic. The almost perfect elasticity of the ether also enters into the question as an important factor.

It is necessary to offer some explanation why, if such action takes place, bodies do not discharge their available energy on contact, and then, if they still exist as matter, fall apart. It is put forward that, as the ether is not perfectly elastic, actual contact never takes place. There is always a thin film of ether left between the bombarding units, and this is sufficient to prevent the discharge of energy. This effect is seen in the case of bouncing soap-bubbles, where air forms the cushion. The air must be under an electric strain for the bubbles to coalesce.

The internal force state of the atom would also under this theory be explained. The action of the inter-atomic particles to a common centre shows that they, too, are influenced by some such attraction; and if this theory be correct they, too, have energy to distribute. It is this that keeps them revolving about a common centre, making up in their total effect the complex or tiny system which we call an atom. This corresponds perhaps to the phase taken up in their turn by molecules, producing what we term the crystalline state. Some such law of movement, be it vortex or otherwise, determines the atom as we know it. According to the above theory, two units approaching each other will ultimately meet; but it is contended that this will never actually take place, because the ether at the speed at which they travel is not perfectly elastic, and a film is always left between the units. Before this can be broken through, the units have separated again, and are under other influences. This takes place before the internal conditions of the unit can be disturbed. In the case of radium it is just possible that the time period is sufficient to allow a slight internal rearrangement of the atom, due to this outside influence, and that this is the cause of the breaking down of the complex unit. This may also apply in some other cases, but to a lesser extent, explaining such a phenomenon as the "Russell effect."

This constant play of forces may also give rise to the vibratory motion of the atoms and molecules in their attempt to break up the complex or vortex in the above mentioned way. This action would also be influenced by the interference of external energy, in the shape of vibrations in the ether itself (heat, electricity, &c.). Accepting the vortex theory, there is no need to assume that the ether is not perfectly elastic. The whirl of the units would itself explain the repelling action. I prefer, however, the former explanation as offering the lesser difficulties.

From this point of view the ordinary molecule is able to

hold its own in this constant bombardment, because of some force common to atoms of a definite nature which connects them up into whirling groups which are, under normal conditions of formation, stable. Chemical reaction, depending on actual contact by solution, pressure, or otherwise, and producing a rearrangement of the atoms, depends on this central molecular force-action being upset by a modification of the ether state surrounding the unit. This must be radical enough to upset the molecular system, but not the closer working system of the atom.

No force that we know of can disturb the internal arrangement of an atom of, say, gold or silver, but, as is well known, some internal or external force is able to do this in one case at least. Arguing from the above theory, it is suggested that it is only necessary to bring about the required state of the surrounding ether in the other cases to accomplish the same end.

Assuming also that the atom has a definite pull corresponding in some way to its system, this in a molecule will determine its external form, be it a whirling complex or otherwise.

Examine the case of the earth and sun from the point of view of this theory. The earth is kept in its course by the fact that the resistance to the flow of energy would be increased if the distance between them was greater, and this would naturally increase as the square of the distance. This is translated into a direct pull, which somehow directly balances the centrifugal force. This extraordinary balancing of these two forces, gravity and centrifugal force respectively, must surely indicate that they are both factors or functions of some unknown but common phenomenon. Otherwise their action and stability is unthinkable unless we are willing to accept the idea of a higher controlling and constant force.

The elliptical path of the earth round the sun would under ordinary circumstances indicate that these two forces, or at least one of them, alternates in phases corresponding to the time duration of progress as expressed in the revolution of the earth.

The effect of attraction, due it is contended to a similar state of affairs, is seen in the case of electrified pith balls. Here they approach one another by distance action to equalise their energy. Why should not gravity be of the same order as this, with the difference that some counter-acting agency prevents the actual "discharge" taking place?

Matter may be the result of the breaking up of the ether into particles of plus and minus values. This is not inconsistent from a mathematical point of view, as their total value in energy would still = 0. Matter simply indicating a difference in potential state of the ether, plus or minus, as the case may be; but for every plus unit there would be a minus one somewhere. In this way the total energy expressed mathematically would not be increased or decreased by what we term the presence of matter. There might be some connection between this and the optically opposite values (+) of some compounds. Nickel and cobalt with the same atomic densities or attractions may have respectively plus and minus values from this point of view.

It is of course the same action which produces the solid state; the space occupied by a certain number of molecules being under existing conditions the least possible permitted by this bombarding action and the vibratory state of the ether. Expansion on heating may also be explained on the assumption that ether is less elastic when in a state of increased vibration. This is the cause of the greater space between the molecules and consequent expansion of the substance.

It is interesting to note in passing the influence of this theory on magnetic phenomena. Assuming that there is a constant flow of energy through space, and that the magnetised iron or the ether which surrounds it is in a state of strain, a better path is offered for this flow of energy, and that consequently this space becomes + to the surrounding district. In other words, more energy streams through this space. If another piece of iron is brought into

this + area, its state will also be modified (as we know), and it would enter into the conducting system and resist any change of position that would break the stream of surplus energy. This explanation overcomes the difficulty of bringing magnetic attraction into line with the theory of the conservation of energy. Some such theory may also account for induction currents. Radium may act in some similar way; the surplus energy being indicated here by increased temperature. This unusual and active state of the ether may be the cause direct or indirect of the breaking down of the radium molecule.

By analogy we might argue that some such state of increased vibration of the ether in the intermolecular space of, say, a silver salt dissolved in a solution which is conducting an electric current, may just determine the difference between a "simple" and a "compound" state for the silver unit; the result of this being deposition of the metal. This extra vibration, by reducing the co-efficient of elasticity of the ether, might tend to separate the atoms making up the molecule, and neutralise in some way the intermolecular attraction. At the other pole it may be that in some way this action is reversed in order that the energy in the system may still = 0.

Surface tension and dissociation in liquid state as examined in the light of this theory are interesting, but the results obtained are reserved for another occasion. Also the bearing of this theory on the idea that energy is only radiated discriminately, and not in all directions or in a promiscuous manner.

The colloidal state taken up by some bodies might possibly be explained in the following way:—The attraction of the molecules of a colloid for each other in the presence of a "dissolving" liquid is not sufficient for the substance to take the solid form. From this point of view a colloid is not a solution at all. Its molecules are so divided, by the interposition of the liquid, that they occupy increased bulk. This gives rise to the swelling action; the pull of gravitation still holds, but to a modified extent. For example, water may be loosely held in combination, or may simply intrude itself, causing the swelling. Gravity still acting, however, the molecules resist parting, and this modified pull is of an elastic nature. On the gradual removal of the "solvent" this loosely held water goes off with the ether, and the substance gradually resumes its normal condition. From a physical point of view a colloid, in the presence of a liquid capable of penetrating it in this way, becomes less rigid, more elastic. Heat may in some cases encourage this action to such an extent that this separation, as measured by the viscosity of the mixture, may be greatly increased. The appearance of the mixture may almost approach that of a solution.

A colloid is never really soluble, but the degree of "hydration" varies with different substances.

The deposition of dye matter in a fibre (colloid) may be due to the fibre substance interfering with this action and reducing the "hydration" of the substance accordingly. This would lead to the deposition of the dye in the substance of the fibre; the rate of precipitation and fastness depending upon factors governing the "solution" and "precipitating" action respectively.

It follows also that the substance dyed must also be a colloid. It, too, must swell up to allow penetration of the liquid carrying the colloid dye or mordant. Perhaps in some such way the explanation of the decomposition of basic dyes may be discovered, the colloid playing the part of the fishing-net, and allowing particles of a certain size to pass with ease, but preventing others. This action, combined with the "fibre action," may be enough to decompose the basic dye with precipitation of the base.

The difference between a colloid and a non-colloid might therefore be a measure of their respective molecular attractions in the dry state, modified by the nature of the "soluting" liquid.

This theory on the face of it gets over the difficulty that gravity acts instantaneously, and does not obey the laws of reflection, refraction, &c. In this way it stands in

advance of the "direct" theories. It is also unnecessary to assume, as in Le Sage's original theory, quite a new state of affairs in the universe to explain its action. It is put forward, however, with the full knowledge that it, in common with all other theories of a speculative nature, may hardly give a correct impression of the true state of affairs as represented by absolute fact. In bringing it forward, and also as an alternative the modified Le Sage's theory, I do so with this full knowledge.

THE USE OF A SOLUTION OF OLEATE OF POTASSIUM FOR THE DETERMINATION OF THE HARDNESS OF WATERS.

By L. W. WINKLER

In the *Zeitschrift für Angewandte Chemie* (1902, No. 31) M. Grittner published a paper in which he declared that the method I had described (*Zeit. Angew. Chem.*, 1901, p. 82) for the determination of the lime and magnesia in waters by means of a solution of oleate of potassium was useless, and that it gave entirely erroneous results when the water contained magnesia. I agree that this method is not applicable when the greatest accuracy is required, or with waters in which the magnesia hardness is greater than the lime hardness; but I will show that this process has considerable merit, even with waters containing a large amount of magnesia, if we operate at sufficient dilutions. Waters rich in magnesia should be diluted until their total hardness does not exceed 5° (German). M. Grittner considers that the froth produced from the titration of the lime is never so characteristic as that which forms when we are dealing with magnesia. I have only been able to observe the contrary so long as the magnesia hardness was not greater than that of the lime. But to do away with this possible inconvenience, No. 1 reagent was improved by the addition of ammonia. The formula we now recommend should therefore be as follows:—Dissolve 6 grms. of pure hydrate of lime and 100 grms. of crystals of Seignette salt in about 250 grms. of water; add about 100 c.c. of ammonia at 10 per cent, and make up the bulk to 500 c.c.

To further examine this new reagent and the method itself, we undertook a fresh series of determinations of hardness. To obtain results as free as possible from errors, the measurements were made by chemists who had not previously used the method. Solution No. 1 was not diluted; Solution 2 was doubled in volume, as was also Solution 3; Solution 4 was tripled; and Solutions 5 and 6 were quadrupled. The results obtained were as follows:—

TABLE I.

Solution No.	Hardness of the solution.			Hardness found.		
	Lime hardness	Magnesia hardness	Total hardness	Lime hardness	Magnesia hardness	Total hardness
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.	3.50	2.50	6.00	3.60	2.57	6.17
				3.75	2.74	6.49
				3.70	2.55	6.25
				8.00	4.80	12.80
2.	8.00	4.00	12.00	8.10	5.40	13.50
				7.84	5.00	12.84
				7.58	7.32	14.90
				8.60	7.12	15.72
3.	8.00	8.00	16.00	8.50	6.98	15.48
				15.15	6.99	22.29
				15.30	7.02	22.32
				15.06	7.77	22.83
4.	15.00	6.00	21.00	16.40	11.20	27.60
				16.84	10.48	27.32
				16.76	11.88	28.64
				21.20	11.80	33.00
5.	16.00	10.00	26.00	20.60	13.60	34.20
				20.32	13.40	33.72
6.	20.00	11.00	31.00			

We see that, in these cases, the results are close, and evidently they would have been better after a little more practice; besides, in none of these cases was the magnesia hardness higher than that of the lime.

The following experiments, carried out with great care by M. Kopper, show the great accuracy that can be obtained, even when the magnesia hardness is high. Solution 1 has not been diluted, Solution 2 was diluted four times, Solution 3 six times, Solution 4 twelve times, Solution 5 ten times, and Solution 6 five times. The results obtained are given in Table II.

TABLE II.

Solution No.	Hardness of the solution.			Hardness found		
	Lime hardness	Magnesia hardness	Total hardness	Lime hardness	Magnesia hardness	Total hardness
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.	4.00	3.00	7.00	4.09	2.83	6.92
				4.07	2.62	6.69
				4.10	2.60	6.70
				10.52	10.68	21.20
2.	4.00	10.00	14.00	4.10	10.60	14.70
				4.07	10.24	14.31
				4.07	10.24	14.31
				27.06	25.00	52.06
3.	4.00	28.00	32.00	27.84	25.02	52.86
				27.54	26.16	53.70
				28.02	28.20	56.22
				28.56	30.18	58.74
4.	28.00	28.00	56.00	28.68	27.06	55.74
				49.80	34.00	83.80
				49.00	33.70	82.70
				49.30	35.20	84.50
5.	50.00	31.00	81.00	6.65	20.75	27.40
				6.85	21.25	28.10
				6.85	21.15	28.00
6.	5.00	22.00	27.00			

The artificial waters examined did not contain any carbonic acid. We have therefore examined the influence of carbonic acid on the results obtained by this method. To effect this, we examined the tap-water of Buda-Pesth before and after saturation with carbonic acid. The results obtained are given in Table III.

TABLE III.

	Without carbonic acid.			With carbonic acid		
	Lime hardness	Magnesia hardness	Total hardness	Lime hardness	Magnesia hardness	Total hardness
1.	7.44	7.48	7.50	7.66	7.60	7.63
2.	2.80	2.81	2.86	2.91	2.99	2.99
3.	10.24	10.29	10.36	10.57	10.59	10.62

As is seen, the presence of carbonic acid, even in large quantities, has little influence; therefore it is unnecessary to get rid of it as a preliminary precaution.

From the above results, I maintain that the method as modified gives good results. The harder and richer the water is in magnesia, the greater is the error; the softer the water, the greater the accuracy. The error is less than one degree with soft waters, two degrees with hard waters, and only a few degrees with very hard waters.

On account of its simplicity, the method can be recommended for the analysis of potable waters, since, from the hygienic point of view, an error of one or two degrees is of no importance. If the water is very hard, an error of a few degrees does not really matter, as the water is no longer potable. The unfavourable case in which the magnesia hardness of the water is higher than the lime hardness, at the same time both being high, is rare. So as to know roughly the proportion of magnesia present a qualitative analysis is made. After a preliminary trial of the total hardness, a second test is made on the lime with water diluted to 5°.—*Zeitschrift für Angewandte Chemie*, 1903, p. 200.

CORRESPONDENCE.

INTERNATIONAL ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—The letter of Professors Sakurai and Ikeda, on the subject of International Atomic Weights, published in your issue of June 24, seems to require a reply. In order to avoid delay, which correspondence with other members of the committee would involve, I venture to make the reply personal. It therefore represents only my own views, expressed without consultation with others.

In the first place, the sub-committee have not argued in favour of the double standard. They have simply recognised an existing demand, and have thought it better to furnish the two sets of values, rather than to leave their calculation to individuals. It is true that in 1900 the larger committee on atomic weights registered a very decided vote in favour of the oxygen standard; but this was followed later by a strong protest from many chemists in Germany and Austria. In the *Berichte* for Dec. 4, 1901, a vote is recorded of 106 in favour of the hydrogen standard, to 78 for O = 16. In other countries a similar difference of opinion exists, less aggressive perhaps, but by no means negligible. The force of this opposition to the oxygen standard was recognised by Landolt, Ostwald, and Seubert in their report for 1901, in which they published a double table; and we have only followed the precedent set by them. We could not properly disregard the wishes of so many distinguished chemists, nor could we assume an agreement where no agreement exists, much as it is to be desired. As for Professor Ostwald's protest, that was promptly answered by Professor Seubert.

The tables published by the present sub-committee have been based upon those issued by Landolt, Ostwald, and Seubert, with only such changes as seemed to be absolutely necessary. The table based upon H = 1 is essentially that issued by the German committee in 1901, with the fewest possible alterations. The objections noted by Professors Ikeda and Sakurai are perfectly just, and represent the evident difficulties attending the use of a double standard. The adjustment of one table to the other is a matter of rather delicate judgment, and the appearance of inconsistency is not always easy to avoid. Just how far a given atomic weight is trustworthy is not certain, and recent researches upon nitrogen and iodine seem to indicate the need of a general revision of the tables in the near future. Sudden or radical changes in the atomic weights are evidently undesirable; but some alterations will have to be made. The recalculation of the hydrogen table may be necessary, however, without delay; and I shall recommend it to the other members of the committee. Final action will depend upon their desires.

With reference to the symbols Gl and Cb, adopted in the American version of our report, a few words seem to be needed. The name glucium and the symbol Gl have clear priority over beryllium and Be, and are favoured by the chemists of France. In England and America the usage is divided; so that here again no agreement exists. I much doubt whether France would accept a change from the older to the newer symbol. In the case of columbium and the symbol Cb, we have again the original nomenclature and notation. Columbium was discovered by Hatchett in 1801. Nearly forty years later Rose thought that he had discovered a new metal, which he named niobium. This proved to be identical with columbium, and the substitution of its name for that first given was wholly unjustifiable. As a matter of scientific nomenclature columbium and Cb are to be preferred.

The reports of the present sub-committee have been published in the journals of the American, English, French, and German chemical societies, and also in several other periodicals. This we have supposed to be an adequate report to the members of the larger body. To report to

over fifty chemists individually would involve much labour, and would seem to be superfluous. I shall, however, take pleasure in sending a copy of our next report to the representatives of the Tokyo Society, in order that it may appear in their journal also.—I am, &c.,

F. W. CLARKE,
Chairman International Sub-committee on
Atomic Weights.

United States Geological Survey,
Washington, D.C., July 12, 1904.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxviii., No. 26, June 27, 1904.

Cyanogen : Solubility and Polymerisation.—M. Berthelot.—The author examines the effect of a number of solvents on cyanogen. In all cases the reaction takes place over mercury, as this gas has no effect on the metal.

Cyanogen and its Action on Potassium Cyanide.—M. Berthelot.—The author operates with various concentrations of potassium cyanide dissolved in water and in alcohol. These solutions dissolve cyanogen rapidly at about 20°. The gas is decomposed and a brown precipitate formed. He finds that water, alcohol, and potassium cyanide cause the destruction of an indefinite number of molecules of cyanogen.

Distillation of a Mixture of Two Metals.—Henri Moissan and M. O'Farrelley.—During a series of researches on the boiling-points of metals, the authors came across examples corresponding to three types of distillation of a mixture of two liquids. Copper and lead behave, when distilled, as a mixture of partially miscible liquids, such as a mixture of ether and water. On the contrary, tin and lead behave as a solution of water and alcohol. Copper and tin resemble a solution of water and formic acid, and there exists in this case a constant temperature—very high, however,—at which the two bodies possess the same vapour tension. The laws which govern the fractionation of two liquids by distillation can be applied also to boiling-points of metals at a very high temperature.

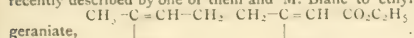
Influence of the Combination of Non-saturated Radicles with certain Molecules on their Rotatory Power. Allylic Ethers of Borneol, Menthol, β -Methylcyclohexanol and Linalol.—A. Haller and F. March.—Continuing their research on rotatory powers, the authors measure the increase in the specific rotation of certain active alcohols when combined under the form of the ether oxide, $R-OCH_2-CH=CH_2$, with a non-saturated molecule like allylic alcohol.

The Red and Yellow Varieties of Thallous Iodide, and the Determination of the Normal Point of their Reciprocal Transformations.—D. Gernez.—The author finds that the velocity of transformation of the two varieties of thallous iodide one into the other becomes less and less as the temperature approaches the normal point of transformation, at which point it is zero. Experiment proves this temperature to be about 168°, i.e., 22° less than Heberling's number.

Thallous Nitrate and Nitrite.—V. Thomas.—The decomposition of thallous nitrate towards 450° produces nitrous anhydride and a well crystalline sesquioxide without an appreciable formation of nitrite. The nitrite decomposes itself in an analogous manner, giving principally nitrous anhydride and thallium protoxide. It seems that the stability of this nitrite is decidedly less than the stability of potassium nitrite. It is also an interesting fact

that thalious nitrate can be partially volatilised without undergoing decomposition.

Total Synthesis of Rhodinol, the Characteristic Alcohol of Essence of Roses.—L. Bouveault and M. Gourmand.—The authors apply the method of synthesis recently described by one of them and M. Blanc to ethyl



geraniate,



This latter substance has been recently synthesised by MM. Barbier and Bouveault. The process is then described by which it is transformed into rhodinol.

Two Homologues of Pyrocatechin.—R. Delange.—The author prepares two homologues of pyrocatechin, ethylpyrocatechin and isopropylpyrocatechin, by methods analogous to those by which he has already obtained propylpyrocatechin.

A New Class of Ether Oxides.—Marcel Descudé.—When hydrochloric acid acts on an aqueous solution of methanal, and the product of this reaction is treated with alcohol, the following compound is formed:— $\text{C}_2\text{H}_5-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_5$, which the author calls dioxymethyldimethylether, a compound boiling at $102-106^\circ$, and of specific gravity 0.864. When methyl alcohol is used, dioxymethyldimethylether is produced, boiling at $106-108^\circ$, and with density 0.959. This body, when in the state of vapour, forms with oxygen a mixture which explodes violently at a red heat. The same phenomenon taking place with the ethylic derivative, but with less intensity.

Methylarsenic.—V. Auger.—Methylarsenic, $(\text{CH}_3\text{As})_4$, is produced when a solution of sodium methylarsinate, sodium hypophosphite, and dilute sulphuric acid are heated together on a water-bath:— $2\text{PH}_3\text{O}_2 + \text{CH}_3\text{AsO}_2\text{H}_2 = 2\text{PH}_3 + \text{CH}_3\text{As} + \text{H}_2\text{O}$. The methylarsenic is a pale yellow oil.

Certain Mixed Phosphorus Derivatives of Hypophosphorous Acid.—C. Marie.—The author prepares a number of mixed acids corresponding to the general formula $\text{R}.\text{CH}(\text{OH})\text{R}'\text{CH}(\text{OH})\text{PO}_2\text{H}$.

Ammoniacal Additive Compounds of Rosaniline.—Jules Schmidlin.—The author prepares a number of additive compounds of rosaniline, and concludes from his experiments that the salts of rosaniline represent non-saturated molecules. The non-saturated functions which they contain are chemically neutral, and can be saturated either by bases or acids. It may be concluded in this case that the non-saturated element ought to be a neutral element, and therefore, in this case, carbon. The limit of saturation seems to be reached with 4 molecules of hydrochloric acid gas or 4 molecules of ammonia.

Bulletin de la Société Chimique de Paris.
Series 3, vol. xxxi., No. 1.

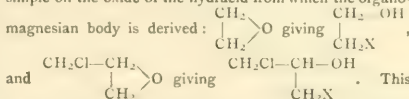
Modifications of the Procedure in Estimating Nitric Nitrogen by the Pelouze-Fresenius Method.—Léon Debourdeaux.—The apparatus used is similar to that of Fresenius, but it comprises an additional condenser, to prevent the concentration and loss of nitric acid. The sample containing the nitrate is placed in the flask, and carbonic acid passed through to drive out the air. The ferrous solution is then passed in, by means of a pipette, through the gas tube, and heat is then applied and maintained until decoloration is complete. The flask is then allowed to cool, still keeping up the current of gas. The tubes are washed with boiled distilled water, and the remainder of the ferrous salt left in solution titrated with a standardised solution of permanganate of potassium. Extraneously close results are found by this method.

A New Method for the Volumetric Estimation of Nitric Nitrogen.—Léon Debourdeaux.—Already noticed.

Colloidal Silver.—A. Chassevant.—Already noticed.

Preparation and Properties of Pure Colloidal Silver.—A. Chassevant.—Already inserted in full.

Action of Organo-magnesium Derivatives of Epichlorhydrine.—André Kling.—As a result of his experiments, the author finds that the organo-magnesium derivatives in the cold react on the ether oxides, giving a compound which, though immediately destroyed by water, furnishes a product resulting from the fixation pure and simple on the oxide of the hydracid from which the organo-



reaction does not take place with the ketones, and thus enables us to differentiate between a ketonic oxidised compound and the oxidic oxygen.

Action of Organo-magnesian Derivatives on Acetone and its Ether Salts.—André Kling.—Already noticed.

Action of Secondary Bases on the Phenolic Carbonates.—M. Bouchetal de la Roche.—The secondary bases of the fatty series attack these carbonates fairly easily, though less energetically than piperidine or dimethylpiperazine. The aromatic secondary bases either do not react at all, or react with difficulty. Dimethylamine and dipropylamine, acting on different phenolic carbonates, have given the corresponding carbamates. The same was the case with dibenzylamine, but the return was bad. The author did not succeed in making diphenylamine react; it does not attack the carbonic ethers, even at 300° .

The Ureas of Piperidine.—M. Bouchetal de la Roche.—Already noticed.

The Organo-magnesium Derivatives of the Dihalogen Aromatic Hydrocarides in the Radicle.—Action of Carbonic Anhydride.—F. Bodroux.—Carbonic acid reacts on the bromides of parachlorophenylmagnesium and parabromophenylmagnesium, giving both a mono substituted benzoic acid and a dihalogen symmetric derivative of benzophenone. If we operate at the temperature of boiling ether, the latter compound dominates; if, on the contrary, we proceed at a low temperature, it is the substituted benzoic acid which forms in the greatest proportion.

Organo-magnesium Derivatives of the Mono-bromised Phenolic Acids.—Action of Carbonic Anhydride.—F. Bodroux.—The author describes the synthesis of anisic acid, paraethoxybenzoic acid, methoxy-2-naphthoic-1 acid, ethoxy-2-naphthoic-1 acid, and propoxy-2-naphthoic-1 acid. The last three are soluble in ether, benzene, acetone, chloroform, and sulphide of carbon, but not in ligroin, even when boiled. They are rapidly decomposed by boiling with a concentrated solution of hydrobromic acid for a few moments. CO_2 is given off, and an ether oxide of β -naphthol is re-formed, which, by the further action of the hydrobromic acid, becomes partially saponified in its turn.

Oxidation of Mixed Organo-magnesium Compounds.—Synthesis of the Phenols.—F. Bodroux.—Already noticed.

Some Compounds of Bismuth with the Oxybenzoic Acids.—Paul Thibault.—The author has prepared the paraoxybenzoate, the β -resorcyate, and the oxyalsicylate in the crystalline form. They all three have the properties of salts of bismuth, and it is to be noted that they can be only prepared by starting with the anhydrous oxide, the hydrated oxide being unattackable. The oxyalsicylate and the β -resorcyate are both stable in water.

Formation of the Azoids.—Reduction of Ortho-nitrobenzyl Ether Oxides.—P. Freundler.—Already noticed.

Comparative Research on the Essences of Geranium of Cannes.—P. Jeancard and C. Satie.—Not suitable for abstraction.

Action of Isocyanate of Phenyl on some Univalent Alcohols. (I).—A. Bloch.—The author has examined the action of isocyanate of phenyl on the alcohols with a large number of carbon atoms to see if the reaction took place under the same conditions as for the lower terms, and if the properties of the bodies obtained were identical with those of ethylphenylurethane. Except with cholesterol, he applied his experiments to the alcohols of the saturated series.

MISCELLANEOUS.

The British Association.—The following papers will be read, amongst others, at the forthcoming meeting of the British Association at Cambridge:—

"On Dynamic Isomerism," by Dr. T. M. Lowry (London).

"The Stereochemistry of Nitrogen," by H. O. Jones, M.A. (Cambridge).

"On Crystal Structure and its relations to Chemical Constitution," by Prof. Paul Groth (Munich).

"On the Velocity of Osmosis and on Solubility: a Contribution to the Theory of Narkosis," by Prof. Isidor Traube (Berlin).

"The Decomposition and Synthesis of Ammonia," by Dr. E. A. Perman (Cardiff).

"On the Energy of Water and Steam at High Temperatures," by Prof. C. Dieterici (Hanover).

"On the Active Variety of Chlorine," by D. L. Chapman and C. H. Burgess (Manchester).

"The Oxidation of Carbohydrates by Hydrogen Peroxide in the presence of Ferrous Sulphate," by R. S. Morrell and A. E. Bellars (Cambridge).

"Studies in the Dynamic Isomerism of the α - and β -Crotonic Acids," by R. S. Morrell and E. K. Hanson (Cambridge).

"A Suggested Explanation of the Phenomena of Opalescence observed in the Neighbourhood of Critical States," by F. G. Donnan (Dublin).

"Sur le Spectre du Soufre Dans la Photographie de L'etincelle des Mineraux," par Mons. le Comte Arnaud de Gramont de Paris.

"Mesoxalic Semialdehyde," by H. J. H. Fenton, F.R.S. (Cambridge).

"Note on the Influence of Radium Radiations on Atmospheric Oxidation in presence of Iron," by H. J. H. Fenton, F.R.S.

"A Reaction for Ketohexoses," by H. J. H. Fenton, F.R.S.

"A Colour Reaction for Methylfurfural and its Derivatives," by H. J. H. Fenton, F.R.S. and J. P. Millington.

"On the Pentavalent Nitrogen Atom," by Prof. Ossian Aschan (Helsingfors).

"Saponarin, a Glucoside coloured Blue by Iodide," by G. Barger (Cambridge).

"The Union of Hydrogen and Oxygen in Contact with a Hot Surface," by Dr. W. A. Bone and R. V. Wheeler (Manchester).

"The Constitution of Phthalein Salts," by Prof. Richard Meyer (Braunschweig).

"The Intensification of Chemical Action in the Neighbourhood of Hot Metals and other Surfaces," by G. T. Beilby (Glasgow).

"Reactions between Solid Salts," by G. T. Beilby.

In his Presidential Address to Section B, Prof. Sydney Young proposes to show that, in attempting to arrive at generalisations regarding the properties of substances, it is advisable in the first place to confine one's attention to compounds (or elements) in which molecular association is not believed to occur. He is considering shortly Kopp's speculations and researches on the boiling points of organic compounds in order to show that Kopp was misled at the outset by dealing with the alcohols, acids, and

esters, and he is suggesting a formula applicable without great error to all organic compounds of normal behaviour except the first two or three members of some homologous series. After touching on the question of molecular volumes Prof. Young considers the behaviour of organic compounds on admixture and the properties of mixtures, more particularly the vapour pressures and boiling points, the relative composition of vapour and liquid, and, lastly, the critical points of mixtures.

Institute of Chemistry of Great Britain and Ireland.

—**Pass List of the July Examinations.**—Of 23 Candidates who entered for the Intermediate Examination, the following 15 passed:—Leslie Hamilton Berry, Thomas William Cheke, Winifred Cox, B.Sc., Reginald Mead Filmer, Charles Gordon Gates, Harry Hurst, Vincent Herbert Kirkham, B.Sc., Jessie Mary Isabel Landon, B.Sc., Archibald William Mairet, Edwin Archibald Maskelyne, William Rest Mummery, Joseph Race, jun., Robert Robison, Robert Thatcher Rolfe, and Samuel Summerson. In the Final Examination for the Associate-ship (A.I.C.), of 8 who entered in Mineral Chemistry the following 5 passed:—David Allan, John Alexander Campbell, David Cowan Crichton, John Gatecliff, jun., B.Sc., and Charles James; one Candidate passed in Metallurgical Chemistry—Thomas Baker, M.Sc.; one Candidate passed in Physical Chemistry—Sydney Herbert Smith, Assoc.R.C.Sc.; of the 5 who entered in Organic Chemistry the following 3 passed:—Robert William Clarke, Bernard Furley Davis, and Edward Charles Martin, B.Sc.; and of 10 who entered in the Branch of the Analysis of Food and Drugs, and of Water, including Examination in Therapeutics, Pharmacology, and Microscopy, the following 5 passed:—Walter Kay Cheshire, B.Sc., Harold Deane, B.Sc., Leonhardt Erich Hinkel, Ernest Gabriel Jones, B.Sc., and Francis Langston Watt, Assoc.R.C.Sc. Two Candidates were examined for the Fellowship (F.I.C.) and both passed:—David Runciman Boyd, B.Sc., Ph.D., and James McLeod. The Examiners in Chemistry were Mr. Walter William Fisher and Professor George Gerald Henderson. Dr. Arthur P. Luff conducted the Examination in Therapeutics, Pharmacology, and Microscopy.

Compounds of Sulphurous Acid Gas with various Salts.—P. Walden and M. Centnerszwer.—With the object of establishing the constitution of the compounds formed by sulphurous acid with various salts, especially with the alkaline iodides, the authors submitted the products resulting from the action of this gas on iodide of potassium, one of which was isolated by Péchard, to a detailed physico-chemical examination (measurement of vapour tension, the curve of melting points, the curve of division into two layers by the elevation of temperature, &c.). From the observations made they were led to the following conclusions:—The melting point of pure SO_2 is -72.7° . The solution of KI in liquid SO_2 gives a deposit, below 0° , of yellow crystals of a compound having the formula $\text{KI}(\text{SO}_2)_4$ fusing at $+0.26^\circ$, in which the SO_2 appears to play a part analogous to that of ammonia gas in the ammoniacal chlorides of silver, for example. At lower temperatures, about -60° , a compound rich in SO_2 is deposited, having the formula $\text{KI}(\text{SO}_2)_{14}$, melting at 23° , and apparently having an analogous constitution. On the other hand, it has not been possible to detect the existence of a compound of the formula $\text{KI}(\text{SO}_2)_2$, by measurements of the vapour tension. The examination of the equilibrium occurring at high temperatures (about 100°) has enabled the authors to determine the higher limit of the existence of solutions of KI in SO_2 . In aqueous solution, a dilution of N/0.4 is sufficient for the complex compounds of SO_2 to be almost entirely destroyed, as shown by cryoscopic measurements. Sulphurous acid gas is more soluble in concentrated aqueous solutions of the alkaline salts, KI, KCNS, RbI, KCl, KBr, $\text{N}(\text{CH}_3)_4\text{I}$, than in water; NaCl is an exception. From these facts it appears that liquefied sulphurous acid, like the two ionising solvents already examined by the same authors

(water and ammonia), is capable of uniting with the binary salts giving complex compounds; these complex compounds appear to exist also in the saline solutions of sulphurous gas; for the sake of simplicity, and by analogy with the terminology used in organic chemistry, the authors propose to call these bodies sulphones; thus the compound $KI(SO_3)_4$ would be called iodide of potassium tetrasulphone.—*Zeit. Physik. Ch.*, vol. xlii., p. 432.

Research on the Dissociation of the Salts of the Heavy Metals. The Nitro-salts of Mercury.—H. Ley and K. Schäfer.—The limit between the acids proper and the neutral bodies which resemble them in some points, such, for example, as the formation of salts, is very difficult to fix. The theory of dissociation alone gives a precise delimitation in this respect; it reserves the title of acids to the bodies capable of forming hydrogen ions. In the same manner the salts are distinguished from the organometallic compounds by their electrolytic dissociation. From this point of view the authors have examined the nitro-salts of mercury, that is to say the mercuric derivatives of the amides and the imides. It has been long known that the dissociation of the mercuric salts depends essentially upon the nature of the bond uniting the metal and the radical. In salts in which this bond is effected by oxygen (the oxidised salts of mercury), the dissociation is very marked; on the other hand, when the bond of union is nitrogen, the dissociation is very feeble; hydrolysis, even at a high temperature is also very feeble; in short, the affinity of mercury for nitrogen is very great. The authors have confirmed these views by examining the decomposition of these nitro-salts by means of strong acids, and by the electrometric measurement of their dissociation. In this way cyanide of mercury behaves in quite a different manner to the imidised salts, from which we may reasonably conclude that the bond between the radical and the metal is not nitrogen but carbon, which has a greater affinity for the mercury than the nitrogen has.—*Zeit. Physik. Ch.*, vol. xlii., p. 690.

Peroxide of Hydrogen of Crystallisation.—Richard Willstätter.—The author has met with several salts susceptible of becoming united, on crystallisation, with a certain number of molecules of peroxide of hydrogen; alum, sulphate of alumina, borax, and acetate of soda are among these. The neutral sulphates of ammonium or sodium also give two exceedingly characteristic compounds. As they easily give up their peroxide of hydrogen (to ether, for example) they can be used in place of this body, as well as in the place of persulphates and percarbonates in a large number of cases, especially when we wish to introduce a definite quantity of peroxide of hydrogen. The compound $(NH_4)_2SO_4 \cdot H_2O_2$ is obtained by the evaporation, in the presence of sulphuric acid, of a solution of sulphate of ammonium and peroxide of hydrogen at 30 per cent. In this manner beautiful crystals are formed having an odour of ozone, efflorescing in air or *in vacuo*, but remaining unchanged in a sealed tube. When heated under reduced pressure a very concentrated peroxide of hydrogen is distilled off. The compound $Na_2SO_4 \cdot H_2O_2 \cdot 4H_2O$ is obtained in a similar manner; in a sulphuric vacuum it loses its water fairly quickly, and then its peroxide of hydrogen slowly.—*Berichte*, vol. xxxvi., p. 1828.

Equilibrium of Solution between Chloride of Silver, Oxide of Silver, and Solutions of Chloride of Potassium and Potash.—A. A. Noyes and D. A. Kohr.—The solubility of AgOH in distilled water, measured in the ordinary analytical manner, is $2.16 \cdot 10^{-4}$ molecules per litre; that of the iodate, $AgIO_3$, is $1.89 \cdot 10^{-4}$ molecules per litre. The ratio of the concentrations of the ions Cl and OH in solutions of KCl and KOH, which at the same time are saturated with AgCl and AgOH, increases by about 8 per cent, when the concentration of the alkaline salts become six times as strong, and then takes the value 0.0000. If we assume that the two argentic compounds are completely dissociated in their saturated solutions, it results from the law of mass action and from the theory of

ions that the ratio of the squares of the solubilities should be equal to the ratio of the concentrations given above, and consequently that the solubility of AgOH in water is ten times greater than that of AgCl. Now, the solubility of AgOH, determined directly by the authors as described above, is 14.4 times greater than that of AgCl determined by Kohlrausch and Rose by electrometric means. It results from this that in saturated solution AgOH is only dissociated in the proportion of 70 per cent. Finally, the authors give a process for the determination of the dissociation of the two salts dissolved in the presence of each other free from uncertain hypotheses; it consists essentially in taking as the figure for the dissociation of each salt in the mixture the figure found for the conductivity of each salt taken alone, at the same concentration, equal to the square root of the product of the concentration of its ions in the mixture.—*Zeit. Physik. Chem.*, vol. xlii., p. 336.

University College, Sheffield.—On the invitation of the Council of University College, the Fifth Chair of Chemistry has been accepted by Prof. William Palmer Wynne, D.Sc. (Lond.), F.R.S., F.I.C., Senior Honorary Secretary of the Chemical Society, in succession to Prof. Carleton Williams. Prof. Wynne is at present Professor of Chemistry in the School of Pharmacy of the Pharmaceutical Society of Great Britain. He has published some 50 papers on the Chemistry of the Naphthalene and Toluene Compounds, all in the *Journal of the Chemical Society*, of which he was the Editor for four years between 1898 and 1902. Prof. Wynne commences his new duties on September 29th next.

UNIVERSITY COLLEGE, SHEFFIELD.

The Council are about to appoint a JUNIOR DEMONSTRATOR in CHEMISTRY. Salary £120 per annum. Duties to begin September 29th next. For further particulars apply to—

W. M. GIBBONS, Registrar.

ASHTON-UNDER-LYNE SECONDARY DAY SCHOOL AND P. T. CENTRE.

The above School will be opened in the Heginbottom Technical School in October next, and the Ashton-under-Lyne Education Committee invite applications for the following Appointment:—

ASSISTANT MASTER, a Graduate in Science with special knowledge of CHEMISTRY. Commencing salary, £120.

It required to assist with Evening Work, the successful applicant will be released from Day School duties for an equivalent period of time.

The Secondary Evening Classes will re-open during September.

Applicants for the above appointment must submit full particulars as to age, education, training, and experience, with copies of not more than three recent testimonials.

Applications, endorsed "Secondary School," must be addressed to the undersigned, and must be received not later than AUGUST 1st.

D. H. WADE, Secretary of Education.

Education Office, Ashton-under-Lyne.

ABSOLUTE ALCOHOL, FREE FROM DUTY, FOR SCIENTIFIC AND RESEARCH WORK IN LABORATORIES

To be obtained from

HUGO LORENZ,
7-8, Idol Lane, Great Tower St., London, E.C.,
Licensed Trader in Alcohol and Spirits of Wine.
Stock kept in suitable packages ready for immediate use

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes,
LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, MINING Lane, London, E.C., who hold stock ready for delivery.

UNIVERSITY OF BIRMINGHAM.

Faculties.—

**SCIENCE.
ARTS.****MEDICINE.
COMMERCE.**SPECIAL SCHOOL OF MODERN LANGUAGES.
DEPARTMENT FOR TRAINING OF TEACHERS.

Schools of—

**ENGINEERING,
METALLURGY.****MINING,
BREWING.****DENTISTRY.**

Leading to Degrees and Diplomas.

The Session 1904-5 commences October 3rd, 1904.

ALL COURSES AND DEGREES ARE OPEN TO BOTH MEN AND WOMEN STUDENTS.

In the Medical School there is a separate Dissecting Room for Women, with a qualified Woman Demonstrator.

Graduates of other Universities may, after two years' study or research, take a Master's degree

SYLLABUSES with all information will be sent on application to the Secretary.

THE

DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided

for Students of both sexes proceeding to the University Degrees in Science, or in Letters, and for the University Diploma in Theory and Practice of Teaching. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 26th. Lectures begin October 4th, 1904.

Prospectuses on application to the SECRETARY.

UNIVERSITY OF GLASGOW.

The Medical Session will be opened on

THURSDAY, OCTOBER 13th, 1904. A Syllabus containing full particulars as to the Course of Education and as to the Preliminary Examination required to be passed by Students before beginning Medical study, may be obtained by applying to Mr. W. INNES ADDISON, Assistant Clerk.

PATENTS, DESIGNS, AND TRADE MARKS ACTS,
1883 TO 1888.

NOTICE IS HEREBY GIVEN that

EDGAR ARTHUR ASHCROFT, of The Birches, Weston (via) Runcorn, Cheshire, seeks leave to Amend the Specification of Letters Patent No. 12377 of 1903 granted to him for "Improved Process and Apparatus for the Production of Metals of the Alkali Group by Electrolysis."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents) issued on July 20th, 1904.

Any person, or persons, may give Notice of Opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

C. N. DALTON,
Comptroller-General.BOULT, WADE, and KILBURN,
Chartered Patent Agents,
111, Hatton Garden, Holborn Circus, E.C.,
Agents for the Applicant.

BRYAN CORCORAN LIM.

MILLSTONE BUILDERS,
WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.Sole Makers of MILBURN'S
Patent Conoidal Stone Grinding Mills.
Especially suitable for certain materials, Water Dry.Works and Warehouses: Back Church Lane,
parcel Dept.: Basement of the Corn Exchange,
31, MARK LANE, LONDON.

RADIUM

(BROM. PUR.)

FROM STOCK

in

1, 2, & 5 m.g.

Tubes.

ON HIRE,

or at

REASONABLE
PRICES.

Pitchblende, from 2/- to 30/- per piece; in Powder, 2/6 per oz.
Kunzite, selected, 2/- per gramme. Carnotite, 2/- per oz.
Aeschynite, 2/- per oz.
Spartite (see NATURE, March 31, 1904, page 523), 2/- per piece.
Chlorophane, 2/- per piece. Samarskite, 2/- per oz.
Zinc Sulphide, green and yellow, 2/6 per tube.
Rad. Residue, 3/- per tube. Polonium, 21/- per gram; 11/- 3/4-gram.
Polonium on Bi. rod, 25/- Willemite, 2/- per oz.
Flexible Bastonite, 3/- to 50/- (See NATURE, June 23, 1904, page 183.)
Monazit, 3/- per oz. Monazit Sand, 1/- per oz.
Diamond chips and powder, 10/- per carat (best quality).
Euklas, Hiddenite, Wagnerite, Phosphite.
Bar. Plat. Cyan., for Screens, 3/- gramme, 60/- oz. Crystals, 4/- gramme. Screens, 9d. per square inch.
Radio-active Screens, 6d. per square inch. Willemite Screens, 6d. per square inch. Electroscopes (special), 21/-.
Sphenariscopes (special), 21/-, 10/6 and 7/6.
Selection of Minerals in Boxes, 2/6, 5/6, 10/6 and 21/-.

NEW ZEALAND VEGETABLE CATERPILLAR; from 2 to 3 inches long, with a stem showing fructification growing out of its head. Specimens may be had from 10/6 to 21/-, according to quality and size.

See NATURE, May 12, 1904, page 44.

Goods may be returned if not approved of, when money will be refunded. Professional Men, Universities, Schools, &c., allowed special terms.

ARMBRECHT, NELSON & CO.

71 & 73, Duke St., Grosvenor Square, W.

E. GEORGE & SONS,
BOOKSELLERS.

161, WHITECHAPEL ROAD, LONDON, E.

Are OPEN to PURCHASE Complete Sets

or short runs of the following:—*Chemical News*, *The Analyst Journal of the Chemical Society*, 1848 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.

MICA.

Telephone
No. 2248
Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., & 103, Minories, E.C., London.

MICA MERCHANTS.

Manufacturers of Mica Goods or Electrical and ALL purposes.
Contractors to His Majesty's Government.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly
Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered
at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC,
As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.Also WHITE LEAD, RED LEAD, CHEMICAL SHEET
LEAD and PIPE, LITHARGE, SHOT, &c.

THE CHEMICAL NEWS.

VOL. XC., No. 2332.

A REVISION OF THE ATOMIC WEIGHT OF BERYLLIUM.*

By CHARLES LATHROP PARSONS.

THE first determinations of the equivalent of beryllium were made by Berzelius in 1815 (*Schweigger's Journ.*, xv., 296), and consisted of a single analysis each of an undoubtedly impure hydrous sulphate and chloride, both of which were probably also basic in character. The results are therefore of no interest in a discussion of the atomic weight of this element.

In 1842, Awdejew (*Pogg. Ann.*, lvi., 106; Clarke's "Constants of Nature," p. 132) carried out an extended investigation on the sulphates of beryllium, and was the first to recognise the neutrality of the hydrous sulphate which Berzelius had considered an acid salt. He also prepared the sublimed chloride by the action of chlorine upon a heated mixture of beryllium oxide and sugar charcoal, and made three analyses of the product which did not show close agreement. They gave an atomic weight approximating 9.8, the high results being unquestionably due to the action of water on the sublimed chloride, as Awdejew dried his gas by simply passing it over calcium chloride. His work on the sulphate was of much greater value. Four results are given, varying from 9.18 to 9.49. The ratio of BeO to BaSO₄ was determined by precipitating the sulphuric acid with barium chloride, removing the excess of barium, and then precipitating the beryllium as hydroxide by ammonia. Apparently no attempt was made to weigh the sulphate itself.

Weeren, in 1854 (*Pogg. Ann.*, xcii., 124), published four determinations obtained from the hydrous sulphate by a method quite similar to that used by Awdejew, except that he precipitated his beryllium hydroxide by ammonium sulphide instead of ammonia, finding it to be somewhat soluble in the latter. His results varied from 9.18 to 9.42.

The following year, Debray published his investigation on beryllium and its compounds, and estimated the equivalent by means of the double oxalate of ammonium and beryllium (*Ann. Chim. Phys.*, [3], xlv., 37; Clarke's "Constants of Nature," p. 133). He determined the oxide by calcination after conversion into the nitrate, and also estimated the carbon in separate samples by an organic combustion. His three results are far from agreeing closely, but the ratio between the two means of BeO : 4CO₂ gave Be = 9.34.

In 1869, Klatzo (*Journ. Prakt. Chem.*, cvi., 235) obtained results varying from 9.13 to 9.40 by means of five analyses upon the hydrous sulphate, using the same method as Awdejew.

Nilson and Pettersen were the next to take up the subject, in 1880 (*Ber.*, xiii., 1451). They had for several years been engaged upon investigations of the rare earths, and had actively taken part in the controversy upon the equivalency of beryllium, which lasted so many years. In fact, they were the first chemists to definitely settle the matter by a determination of the vapour-density of beryllium chloride, and, quite contrary to their previously held opinion, to establish its bivalency. In this atomic weight work they first attempted to use the sublimed chloride, but abandoned the trial upon finding calcium in their product, and their glass tube apparently attacked. They then resorted to the crystallised sulphate, as all previous investigators, except Debray, had done, but used an entirely different method, weighing the sulphate itself after pulverising the crystals and pressing between filter-

paper, then igniting in platinum, and weighing the oxide produced. Their sulphate, too, was probably purer than any previously made, having been produced from the sublimed chloride. Their four results agreed very closely, 9.09 to 9.114.

Krüss and Moraht published their well-known investigation in 1891, their results also being obtained upon the hydrous sulphate, which they dried over phosphorus pentoxide before weighing (*Liebigs Ann. Chem.*, cclxiii., 38). Their sulphate was derived from three different sources, and was very carefully purified. They also used very much larger amounts of the sulphate for each ignition than any other investigator had done, which compelled them, however, to blast their specially constructed platinum crucible for unusually long periods of time. They made fourteen closely agreeing analyses, their results varying between 9.02 and 9.088.

All results upon the atomic weight of beryllium obtained up to the present time are therefore based upon analysis of the hydrous sulphate BeSO₄·4H₂O, with the single exception of Debray, who used the double oxalate Be(NH₄)₂(C₂O₄)₂, and may be summarised as follows:—

	Ratio determined.	Mean. O
Awdejew	BeO : BaSO ₄	9.34
Weeren	BeO : BaSO ₄	9.27
Klatzo	BeO : BaSO ₄	9.28
Debray	BeO : 4CO ₂	9.34
Nilson and Pettersen . .	BeSO ₄ ·4H ₂ O : BeO	9.104
Krüss and Moraht . . .	BeSO ₄ ·4H ₂ O : BeO	9.05

Balance and Weights.

The balance used in the analyses which follow was a new No. 1 Staudinger, which was bought especially for this work. The adjustment was so arranged that a difference in weight of 1 m.grm. caused a deflection of twenty divisions on the scale, which could easily be read to 0.2 of a division by means of the microscope attachment. The balance was placed in a second case, enclosed on all sides, and large enough to permit of convenient manipulation when the front was lifted. This case was attached directly to a brick wall two feet thick, with a shallow air space between the case and wall, and without any floor connection, so that it was not subject to any ordinary jar. It was situated in an evenly heated room. All weighings were made by the method of substitution against a tare consisting of a light thin glass weighing-bottle, containing a platinum crucible and cone of the same size and shape as those used in the analysis. This tare was treated in all respects the same as the weighing-bottles against which it was balanced, and both, on removal from the desiccator, were wiped with a soft cotton-cloth and allowed to stand in the inner balance case. This case was kept as dry as might be by means of sulphuric acid.

The weights were of brass, platinum-plated, and were compared individually and against a standard weight by the Kaiserl. Normal-Aichungs Kommission. I also compared them against each other, and my comparisons agreeing closely with those certified to by the commission, their figures were accepted as correct. All weighings were corrected to a vacuum standard.

I. Preliminary Investigations.

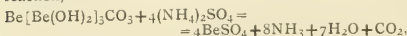
The Preparation of Material.—The beryllium compounds used in this investigation were derived from two sources—the first being beryl from Grafton, N.H., and the second Kahlbaum's "Berylliumhydrat."

Beryl is most readily and quickly attacked by fusion with sodium hydroxide, but no container could be procured which was not also acted upon to such an extent as to render it useless. Nickel crucibles on the market are too small to be of use except for analytical purposes, as the fused mass foams badly. The method of Lebeau (*Comptes Rendus*, cxxi., 461), who proposes the high heat of an electric furnace to volatilise a portion of the silica of the

* From the *Journal of the American Chemical Society*, xvi., No. 7.

beryl and render the residue easily decomposable by acids, has distinct advantages to those possessed of the necessary facilities. Beryl itself is not affected by any acid, even hydrofluoric, and this fact renders a separation from orthoclase and quartz, which most of the large New Hampshire beryls contain, an easy matter.

After a careful study of the many other methods for the decomposition of beryl the following procedure was adopted as the most convenient in my laboratory:—The powdered beryl was fused in a Battersea crucible with a mixture of sodium and potassium carbonates, and the fused mass turned out to cool on a smooth iron plate. The melt was pulverised and washed with water, which removed soluble sodium and potassium salts, notable amounts of silica, and some beryllium, but the loss was more than compensated for by the greater ease of the subsequent operations. The moist residue was just barely covered with water and concentrated sulphuric acid added in excess, by which procedure it became at once a dense jelly-like mass, which was easily broken up, dried, and heated on a sand-bath to render silica insoluble. The fine, nearly white and dry powder so produced was washed with hot water, potassium sulphate added to the solution, and the major part of the aluminum crystallised out as alum. The mother-liquor was oxidised with potassium chlorate and sodium carbonate carefully added in small portions at a time with intermediate boiling until the filtered solution was colourless. Most of the remaining iron and aluminum are thus precipitated before the beryllium, as Hart has pointed out (*Journ. Am. Chem. Soc.*, xvii., 604), and the selective action is undoubtedly due to the power which beryllium sulphate has of dissolving considerable amounts of its own carbonate. To the filtered solution sodium carbonate was added with care to avoid any great excess, as the precipitated basic beryllium carbonate is notably soluble in sodium carbonate solution, and the precipitate washed to remove sodium salts. It was then dissolved in excess of sulphuric acid, and the $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ crystallised out on evaporation. After a second crystallisation from pure water the sulphate was again dissolved, precipitated by ammonia, filtered, and washed, without any attempt, however, to free the gelatinous hydroxide entirely from sulphates. The removal of the main part of the ammonium sulphate is advisable, however, as the reverse reaction,—



takes place to a greater or less extent on continued boiling, after precipitating the basic carbonate from ammonium carbonate solution, and is, of course, proportional to the amount of sulphate present. The reaction may be easily complete if excess of sulphuric acid is present before neutralisation. The beryllium hydroxide was transferred to a large bottle, covered with an excess of dilute ammonia, and carbon dioxide passed through the liquid. When nearly saturated, more ammonia was added, the carbon dioxide shut off, and the bottle allowed to stand in a warm place with occasional shaking. The liquid was filtered from some undissolved aluminum hydroxide, and was treated with excess of ammonium sulphide, as recommended by Scheerer (*Journ. Prakt. Chem.*, [1], xxvii., 76) and Krüss and Moraht (*Liebigs Ann. Chem.*, cckxii., 47). A small amount of a black precipitate was invariably thrown down at this stage. After standing for several days, the solution was filtered, with special care that the black precipitate was at all times in contact with liquid containing ammonium sulphide. It was then boiled with constant stirring until ammonia was evolved and precipitation was complete. Vigorous stirring of some form is absolutely necessary as the granular precipitate settles quickly, and causes violent bumping, which I have never been able to prevent by any other method. The basic carbonate thrown varies continually in composition as precipitation progresses, but the final product has the approximate formula $\text{Be}[\text{Be}(\text{OH})_2]_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ when dried over sulphuric acid.

It is slightly soluble in water, so precipitation is never quite complete. At 100° it loses about 4.50 per cent of water, and contains about 44 per cent of BeO . Like all the basic compounds of beryllium which have come under my observation, except those of the acetate group to be described later, its composition is by no means definite. The carbonate was twice re-dissolved in pure sulphuric acid, and re-precipitated from ammonium carbonate as described above, except that the treatment with ammonium sulphide, although each time repeated, failed to separate any further black sulphide.

Kahlbaum's "Berylliumhydrat" contained quite notable amounts of aluminum and small quantities of iron. It was precipitated three times as basic carbonate, exactly as described above, and the small amount of dissolved iron thrown out by ammonium sulphide.

The basic carbonates so prepared were employed as a basis for the production of the purer salts used in the atomic weight determinations. They contained small amounts of aluminum, but were free from other admixture.

The Ammonium Sulphide Precipitate.—Krüss and Moraht lay special stress upon the removal of the black precipitate formed by adding ammonium sulphide to the ammonium carbonate solution, and attribute the fact of their low results to its removal. In fact, their investigation was undertaken with this idea in view. According to them the precipitate was not due to iron, but, while yielding a black sulphide, gave a white hydroxide (*Liebigs Ann. Chem.*, cckxii., 47). They promised further investigation. Apparently unknown to them Scheerer had, on July 15, 1842 (*Journ. Prakt. Chem.*, [1], xxvii., 76; *Pogg. Ann.*, September, 1842), read a paper at Stockholm in which he recommended the same procedure for the removal of the small amount of iron dissolved in the ammonium carbonate, and Vauquelin, in one of his early articles (*Allg. Journ. dt. Chem.*, i., 595), speaks of the difficulty of removing the last traces of iron, but says it can be done by means of potassium hydrosulphide. This must have been done in ammonium carbonate solution.

The matter has been one of interest to chemists working on beryllium and its compounds since the article of Krüss and Moraht was written, for it appeared to follow that, if their statement of a black sulphide and white hydroxide was true, a new element was under consideration. As the amount of precipitate is small, I began some three years ago, in the early part of my work on beryllium, and while working on beryl, to save the small amounts of black precipitate obtained with each new lot of material. Fortunately, I did not realise for some time the desirability of removing the ammonium sulphate previous to solution in ammonium carbonate, so that the filtering of the ammoniacal solution after precipitation of the hydroxide was omitted. In this way about a gram. of the black precipitate was collected, and on analysis it proved to be a mixture of the sulphides of iron and zinc, but mainly zinc. On adding ammonia, with care to avoid excess, it yielded a precipitate which, in small amounts, might easily have been called white, while on addition of ammonium sulphide the black iron sulphide immediately predominated. Over 0.5 gram. of zinc oxide was separated in the pure state, and was procured from several kilograms. of beryl. I believe the presence of zinc in beryl has not before been noted.

The "Berylliumhydrat" was also carefully examined, and the presence of zinc established, but in very small amounts. It is quite probable that this material had been washed from alkaline solution, which would, of course, have removed the greater part of the zinc.

Beryllium Chloride.—It is quite generally conceded that atomic weight determinations based upon the analysis of the metallic halides, are among the most accurate made, and it is highly desirable that the beryllium equivalent be determined on the pure chloride. Unfortunately, however, it has properties which render the task extremely difficult, being immediately acted upon by the slightest trace of water, and according to Nilson and Pettersen (*Ann. Chim. Phys.*, [5], xiv., 428), and Humpedge (*Proc. Roy. Soc.*,

xxxix., 1) it attacks glass. In my earlier studies on the subject I had hoped to be able to purify the chloride by the same method that Richards used for magnesium (*Zeit. Anorg. Chem.*, xiii., 92), by evaporating carefully a mixture of the chlorides of beryllium and ammonium in a perfectly dry current of hydrochloric acid gas, and subliming off the ammonium chloride. Early experiments showed that the ammonium chloride did prevent the decomposition of the beryllium chloride, and a dry mixture but little, if any, decomposed could be obtained. On heating, however, they both sublimed together, and no separation could be made, in spite of the fact that Carnelley places the melting-point of beryllium chloride as between 858° and 890° (*Phil. Mag.*, [5], xviii., 21). If the mixture be dried and heated in air, the ammonium chloride alone sublimes, leaving the oxide of beryllium in so light and feathery a form that it is carried by air currents about the room.

The normal chloride, bromide, and iodide were first made by Wöhler by heating a mixture of the oxide and carbon in the appropriate gas, and subliming the product (*Ann. der Phys.*, xliii., 577). The chloride was also made from the metal itself by sublimation in dry hydrochloric acid gas by Nilson and Pettersen. Lebeau has recently prepared the iodide from the carbide in a similar manner (*Comptes Rendus*, cxcvi., 1272). The chloride and iodide have quite similar properties. The bromide has been little studied. All are attacked violently by water with evolution of the corresponding acid. The solution of the chloride is strongly acid in reaction, readily dissolves the carbonate or loses hydrochloric acid on evaporation. Evaporation on the water-bath or *in vacuo* by sulphuric acid has, in my hands, invariably yielded basic compounds. I have made many analyses of these basic chlorides, but no two products have ever agreed in composition, nor has crystalline structure ever been observed. Heating to a high temperature yields the pure oxide, but a small amount of BeCl_2 seems to be always sublimed after the last traces of water have been driven off. Every attempt to make the compound $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$, described by Awdejew, met with failure. No crystalline chloride of any degree of hydration could be prepared. I believe the existence of this compound to be highly improbable. Some recent experiments have led me to seriously doubt the conclusion of Nilson and Pettersen, and Humpedge, as to the action of BeCl_2 on glass, at least upon Jena or hard potash glass, in both of which I have sublimed the chloride from place to place, and repeatedly from the same place, without the slightest sign of action so long as all moisture was absent. The least moisture, however, caused a thin film of the oxide to form, which might easily be mistaken for corrosion, and which adhered tenaciously to the glass.

Beryllium Sulphate.—Beryllium forms two normal sulphates, $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{BeSO}_4 \cdot 2\text{H}_2\text{O}$, which are definite in composition under proper equilibrium conditions. As will be shown in another paper soon to be published, the sulphate $\text{BeSO}_4 \cdot 7\text{H}_2\text{O}$, described by Klatzo (*Journ. Prakt. Chem.*, cvi., 233), does not exist, and it is doubtful if the anhydrous sulphate BeSO_4 has ever been prepared pure. It is upon the tetrahydrate that the accepted atomic weight of beryllium rests. The dehydrated salt is produced from the tetrahydrate by heating at 100° , and is apparently stable in dry air below this temperature. It was an intermediate step in the work of both Nilson and Pettersen and Krüss and Moraht, and would have given a second ratio for the determination of the equivalent.

In the early stages of my work on the sulphate it became apparent that I could not dry the normal tetrahydrous salt over phosphorus pentoxide as Krüss and Moraht had done, for the material slowly but continuously lost in weight. No absolutely definite point could be taken as representing exactly the salt $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, although the powdered crystals are stable at ordinary temperatures and pressures when air-dried. Under these conditions they probably are as near to the accepted formula as is the case with most hydrous salts. Nilson and Pettersen seem to have recognised this fact, for they made no attempt to dry their

air-dry material other than by pressing between filter paper. To establish more definitely the instability of the water of crystallisation I undertook a series of tensimeter experiments. With phosphorus pentoxide as the desiccating agent, the water of crystallisation of the tetrahydrous salt shows a pressure of 20 m.m. olive oil at 20° , and this pressure increases rapidly as the temperature of the thermostat rises. The pressure in the tensimeter was many times equalised and the experiment repeated. Weeren (*Ann. der Phys.*, xcii., 124) states that $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ loses one-third of its water at 35° . The dihydrous salt $\text{BeSO}_4 \cdot 2\text{H}_2\text{O}$, while for all ordinary purposes stable at 100° , appears to very slowly lose its water of crystallisation if continuously maintained at this temperature. I have never been able to obtain the same equivalent from the weight of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ taken and the weight of $\text{BeSO}_4 \cdot 2\text{H}_2\text{O}$ derived therefrom. One would naturally suppose, since Krüss and Moraht first dried their salt to slowly remove the first 2 molecules of water before ignition, that they arrived at a like conclusion. This fact in itself should, in the absence of other proof of definiteness of composition, render the use of either for atomic weight purposes subject to question.

In order to repeat the work of previous investigators on the sulphate, I prepared a quantity of a very pure salt by first dissolving the carbonate, already mentioned, in hydrochloric acid and treating according to the method of Havens (*Zeit. Anorg. Chem.*, xv., 18) to remove any aluminum remaining. During the course of this work it was discovered that if the filtered saturated solution of beryllium chloride in the ether hydrochloric acid mixture was cooled down or supersaturated, a mass of beautiful white needle-like crystals were formed, which could be separated from the mother-liquor by means of a Buchner funnel without the use of filter-paper. These crystals contain all the constituents of the solution—beryllium chloride, hydrochloric acid, ether, and water. Their exact composition is yet to be determined, but as they seemed to offer a further means of purification, all of the beryllium chloride used in the preparation of the sulphate was passed through this medium. On exposure to air the crystals were decomposed, losing ether and hydrochloric acid. The purified material was dissolved in excess of ammonium carbonate, boiled, precipitated, and washed free from chlorides and ammonia. The carbonate so produced was dissolved in slight excess of carefully purified sulphuric acid. On evaporation, crystals of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ were obtained, which were four times crystallised from water, washing each time with absolute alcohol. The crystals so prepared were dissolved in pure water, evaporated to the crystallising point, and the viscous hot solution poured into a large excess of strong alcohol. No precipitation occurred at once, although a milky, apparently colloidal, solution was produced, which, on standing over night, crystallised out almost completely. This was repeated once, and the crystals so obtained were dissolved in carefully purified water, evaporated, and crystallised as small crystals by stirring. When air-dry they were powdered and used for determination of the equivalent and for the experiments already briefly described. Determinations were made on both the air-dried sulphate and upon sulphate which had been, for a short time only, over phosphorus pentoxide. The sulphate was weighed into platinum crucibles, dried at 100° , re-weighed, and dried at a gradually increasing temperature in a Jannasch beaker until the remainder of the water and most of the sulphur trioxide was removed. It was then blasted to complete removal of the sulphur trioxide. This required a very high temperature and was not complete, with the blast at my command, if the platinum crucible was protected by enclosure in a second. Fortunately, however, the oxide produced from the sulphate did not in the least adhere to the platinum crucible. The final weight of the crucible was, therefore, taken in determining the weight of the oxide. Nilson and Pettersen, and Krüss and Moraht both blasted platinum direct and mention no correction therefor. It would seem likely, however, that Krüss and Moraht made such a correction, for they speak of having to

diminish the weight of the platinum crucible used as a tare in order to balance the one used in analysis. They used such large amounts of material that this error would be comparatively small in their results.

It has not been deemed necessary to enter into details of manipulation, but full precautions were observed, as described in the analyses to follow. Results on the sulphate yielded atomic weights from 9.18 to 9.36. Sources of probable error were so apparent that I had no confidence in the results obtained, and they will not be included in the final summary. The work is described for its bearing on the investigations of others, and to call attention again to the probable errors in using a hydrous salt as a basis for the determination of atomic weight. Unfortunately, until quite recently, no other salt seemed to be available in the case of beryllium.

(To be continued).

NOTE ON THE URINE OF A TORTOISE.

By L. DE KONINGH.

THIS very clear specimen had a faintly acid reaction. Total solids, 1.03; ash (nitrated), 0.63 per cent. On heating the residue, a slightly aromatic, but not at all offensive odour, was noticed. The ash was slightly phosphatic. The urine gave no precipitate with picric acid, but a strong darkening on applying the bismuth test for sugar; the usual precipitate was not noticed.

After being kept in a test-tube for two days the sides were coated with a transparent crystalline deposit, which was found to be insoluble in strong acetic acid, but which gave the murexide reaction.

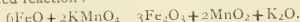
The liquid poured off from the deposit was tested in a nitrometer with excess of alkaline bromine solution. 1.4 c.c. of the urine yielded only 0.2 c.c. of gas.

THE IODOMETRIC ESTIMATION OF IRON IN THE FERRIC STATE.

By R. NAMIAS AND L. CARCANO.

THE volumetric estimation of iron is almost always carried out in solutions in which the iron is in the ferric state. With the ordinary permanganate method it is important to have only sulphuric acid present, because under all conditions hydrochloric acid has an action on the permanganate that cannot be overlooked; it is difficult to observe the end of the reaction accurately, since the colour obtained, after having oxidised the whole of the ferrous salt, disappears rapidly. With a view to avoiding the long operation necessary for the elimination of the hydrochloric acid, we can make use of Penny's method, in which we use a titrated solution of bichromate, and the touch method with a solution of ferricyanide of potassium, to find the exact moment at which the blue colour of the ferrous ferricyanide ceases to be formed. The method devised by Namias (*Moniteur Scientifique*, Feb., 1900) is much preferable, but it is little known although it is very exact.

This method is founded on the estimation of the ferrous salt in neutral solution (containing pure oxide of zinc in suspension) by permanganate of potassium. Under these conditions the reaction does not take place, as in acid solutions, between 10 atoms of iron in the ferrous state and 2 molecules of permanganate, because in this case the reduction of the permanganate stops after the formation of the MnO_2 . This method depends on the following simplified reaction:—



As will be easily understood, this method enables us to neglect entirely the nature of the acid combined with the iron, provided we have not to do with a reducing organic

acid. The operation should be carried out warm so as to deposit the oxides and to observe when the liquor commences to turn red. One of the most persistent drawbacks of all the methods in which the iron is estimated volumetrically in the ferrous state, is the necessity for reducing the ferric salt to the ferrous state. With this operation, besides losing a great deal of time, we have the further drawback that the impurities contained in the zinc, especially the small quantities of iron, may cause an error which is often important and never negligible, as we have proved.

We have not found any zinc, supplied as very pure, which after solution will not reduce a little permanganate; it is necessary, therefore, to calculate with the greatest accuracy the amount of permanganate reduced by a known weight of the zinc. The utility of a method which will enable us to estimate the iron in the ferric state directly, and by volumetric means, is evident, especially when we are dealing with the analysis of lime, slags, iron ores, refractory materials, &c.

We can safely say that up to the present there is no method known by which iron can be determined volumetrically and accurately in the ferric state.

The method based on the use of stannous chloride is very inconvenient, and not to be depended upon, because of the rapid variation of the strength of the solution of stannous chloride, even when kept in special apparatus.

The method founded on the reduction of the ferric salt by hyposulphite of sodium in the presence of a salt of copper, is inaccurate also, as was recognised by Fresenius, and it requires very careful manipulation.

The only method which is very simple and rapid in practice, and looked upon as exact, is the one founded on the following reaction:—(1) $Fe_2Cl_6 + 2KI = 2FeCl_3 + 2KCl + I_2$.

This method, examined by Mohr and Braun, is considered by Fresenius to be practically accurate. We have followed the instructions of Fresenius closely, and we have also endeavoured to modify them as far as time, the dilution of the liquid, and acidity is concerned, but in no case have we obtained accurate or even approximate results. This can be seen in the table of results we give at the end of this article.

We are convinced that the principal reason for the inaccuracy of the method must be attributed to the great facility with which the inverse reaction takes place, that is to say:—(2) $2FeCl_3 + 2HCl + I_2 = Fe_2Cl_6 + 2HI$.

Thus, it is evident that if we could remove a great part of the iodine set free, the reaction would take place quantitatively. We first of all tried to get rid of the greater portion of the iodine by heating the solution to boiling in a current of carbonic acid, and collecting the iodine in a solution of iodide of potassium, and estimating both the iodine given off and that remaining. The results approach the truth closely, but they are too low.

We next endeavoured to remove the greater part of the iodine by means of a small quantity of chloroform added to the solution, and this is the method that gave us the best results. These results are very accurate and are such that no other method for the volumetric determination of iron can surpass.

The following is briefly our method of proceeding:—

The solution containing the salt of iron, oxidised with nitric acid, is evaporated to dryness with an excess of hydrochloric acid; the residue is dissolved in the smallest possible quantity of hydrochloric acid. The solution is diluted with water until it contains about 1 or 2 per cent of iron.

The solution is almost completely neutralised with carbonate of soda, add concentrated hydrochloric acid until about 5 to 10 per cent of acid is present, then add 5 or 10 c.c. of pure chloroform. Leave for several hours, twelve if possible, in a closed matras, shaking occasionally. The iodine set free is estimated with a titrated solution of hyposulphite of sodium in the presence of starch emulsion.

It is necessary to make a blank experiment with the same quantity of chloroform and iodide of potassium dissolved

in a small quantity of water, and treated with the same amount of hydrochloric acid as is used in the actual analysis. In this manner we find that a small quantity of iodine is always set free under these conditions; naturally this iodine should be subtracted from the total iodine. We have attempted to apply an analogous method to the estimation of copper in the state of cupric chloride, and we have obtained satisfactory results. We shall make further experiments with a view to finding the best conditions for applying the method to this case.

Solution of Ferric Chloride containing 1 per cent. of Iron, slightly Acid.

	Fe per cent.
10 c.c. with 24 grms. of iodide of potassium: left for twelve hours in the cold ..	81.00
Heated in a matras, containing a solution of iodide of potassium, and titrated immediately ..	75.00
Ditto ditto, after standing two hours ..	74.00
With the addition of acetate of soda in the cold	69.06
Distillation of the greater portion of the iodine in a current of carbonic acid ..	93.08
Acidulated with a drop of concentrated hydrochloric acid, treated with chloroform, and left for twelve hours in the cold ..	98.52
With 1 c.c. of hydrochloric acid, and left for twelve hours ..	99.6
The same repeated ..	99.6
Repeated, but without standing ..	90.0
Add 1 c.c. of hydrochloric acid, left for nineteen hours ..	99.3

The iron used for these estimations was pianoforte wire, which might contain 0.3 to 0.4 per cent. of impurities (C and Mn).—*Moniteur Scientifique*, vol. xviii., April, 1904.

CONSTITUTION OF NITRIC PEROXIDE.

By EDWARD DIVERS, M.D., D.Sc., F.R.S.,
Emeritus Professor of Chemistry, Imperial University of Tokyo.

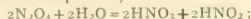
In a paper appearing in the *Journal of the College of Science, Imperial University, Tokyo* (vol. xix., Article 15), Haga has demonstrated that Fremy's sulphazilate is an oximeperoxide and a tervalent nitrogen compound. If Hantzsch and Semple's suggestion is accepted (*Ber.*, 1895, xxviii., 2744; cf. Piloty and Schwerin, *Ber.*, 1901, xxxiv., 1884 and 2354), that Fremy's salt is also a sulphonated nitric peroxide, it follows that the constitution of nitric peroxide is at last determined, being that of nitrosyl peroxide. Hantzsch and Semple must be right, for, after Haga's researches, a sulphazilate as a peroxylaminesulphonate cannot be supposed to be other than a sulphonated nitric peroxide. It only remains, therefore, to show that nitric peroxide is a true peroxide in its chemical relations.

It is formed from nitric oxide and oxygen, just as sodium peroxide is formed from sodium and oxygen. Nitrous acid cannot, indeed, be shown to pass simply into it and back again, as a hydroxylaminedisulphonate (sulphonated nitrous acid) changes into a peroxylaminesulphonate, but that is only on account of its own instability and that of nitrous acid.

Its interaction with organic oximes, in which it converts these substances into peroxides and becomes hydrogenised into nitrous acid (Scholl), is in accordance with its nature as a true peroxide. Similarly, it converts a hydroxylaminedisulphonate into a peroxylaminesulphonate (Haga).

Nitrosyl peroxide and a peroxylaminesulphonate both interact with water in essentially the same way, the apparent difference being due to the limits imposed by the sulphonation in the case of the latter substance. The former yields half its nitrogen as nitric acid and half as nitrous acid, whilst the latter yields half its nitrogen as a mixed anhydrosulphate (hydroxylaminetrisulphonate) and

the other half as nitrous acid and sulphonated nitrous acid (hydroxylaminedisulphonate):—



It would seem, therefore, that wholly on the evidence afforded by Haga's work, it can now be confidently asserted that dinitric peroxide is nitrosyl peroxide and a compound of exclusively tervalent nitrogen. The constitution of mononitric peroxide, in regard to these two points, remains to be considered, but can hardly be very different.

Hantzsch and Semple have suggested (*loc. cit.*) that the bluish-violet dissolved form of a peroxylaminesulphonate corresponds with mononitric peroxide, and its crystalline form with dinitric peroxide. Since then, Piloty and Schwerin (*loc. cit.*) have expressed the belief that porphyrexide, which has the colour of mononitric peroxide, may also be a derivative of this peroxide, because it contains the group :NO singly, as shown by the formula $(\text{C}_5\text{H}_5\text{N}_3):\text{NO}$. Its molecular weight, however, has been only indirectly ascertained, that is, by cryoscopic determinations of those of its nitrate and its chloroderivatives. That its molecular weight is not double as great is a remarkable fact, for, in its chemical behaviour, and especially in its reversible relation with porphyrexine $(\text{C}_5\text{H}_5\text{N}_3):\text{NOH}$, porphyrexide seems to belong to the class of oximeperoxides. Piloty and Schwerin do not indeed recognise this, and have instead come to the conclusion that the nitrogen of the group :NO in porphyrexide and in mononitric peroxide must be quadrivalent. In the light of Haga's experimental results, this view of the matter has become untenable, since porphyrexide and the peroxylaminesulphonates appear to belong to the same class of nitroso compounds, as Piloty and Schwerin themselves have pointed out.

In the few cases in which it has been possible to determine cryoscopically the molecular weight of a glyoximeperoxide, this has been found to include :NO twice. This result may be owing to the glyoxime constitution of these peroxides, but even so there is still no peroxide, except mononitric peroxide, and possibly porphyrexide, the molecular weight of which is such that it contains the group :NO only once. The occurrence of many nitroso-compounds in a colourless, solid form, and in a bluish-violet liquid form, does not lend much assistance in deciding the molecular weights of the two forms of a peroxylaminesulphonate, since they contain not :NO but :NO. But it must not be left out of sight that Piloty (who thinks otherwise, and has been followed by Schmidt, Bamberger, and others) has succeeded in showing that the white form of these compounds contains the group :NO twice, and that the deeply-coloured modification contains it only once. But here the latter is the form which must be treated as the chemically active one, whilst the double weight found for the white form has to be left uninterpreted chemically, as, for example, in the case of the formula $(\text{C}_5\text{H}_7\text{NO})_2$ for nitroso-octane.

In the paper by Hantzsch and Semple (*loc. cit.*) there occurs, but in a footnote only and without comment or explanation, the punctuated formula $\text{O}:\text{N}:(\text{SO}_3\text{K})_2$; whether this is to be regarded as a printer's error for $\text{O}:\text{N}:(\text{SO}_3\text{K})_2$ is uncertain, but if it is not it indicates some recognition by these chemists of the presence of univalent oxygen. However this may be, the possibility of the nitrogen being quadrivalent being inadmissible, the only solution of the matter seems to be to consider that both mononitric peroxide and porphyrexide are compounds of univalent oxygen, although still peroxides. The fact that a molecular quantity, such as that formulated by $\text{HO} \cdot \text{NO}_2$, $(\text{SO}_3\text{K})_2\text{NO}$, or $(\text{C}_5\text{H}_5\text{N}_3)\text{NO}$, is never met with singly in chemical interactions militates against the acceptance of this explanation. Piloty and Schwerin, in discussing the quadrivalency of nitrogen, conceal this fact by stating that porphyrexide is produced from porphy-

rexine by the action of *half an atom* of oxygen. It is much more correct to hold with Haga that the molecule of peroxylaminesulphonate, and therefore also of mononitric peroxide and of porphyrine, is not less than that represented by $[\text{NO}(\text{SO}_3\text{K})_2]_2$, $(\text{NO})_2$, or $(\text{C}_5\text{H}_7\text{N}_2\text{O})_2$. as the case may be, if by molecule is meant the smallest chemically active weight of a substance. But still the fact remains that, when measured by comparison of their physical properties, the molecular weights of porphyrine and red nitric peroxide are expressed by half the above formulae, and probably the bluish-violet form of a peroxylaminesulphonate has also a molecular weight, which when physically considered, should be expressed by the formula $\text{NO}(\text{SO}_3\text{K})_2$. These weights, only physically determined, have no chemical significance, and should be distinguished from their doubles, the truly chemical molecular weights. But, as pseudochemical molecules, they must be represented to contain a univalent atom of oxygen.

It is, after all, not so difficult to admit that oxygen may be univalent in a peroxide. In fact, true peroxide may be defined and differentiated from other oxides, as being a compound in which some or all of the oxygen is exerting on the rest of the compound only half its usual valency. Or, conversely, a peroxide may be defined as a compound containing oxygen which is either actually univalent or exteriorly and quasi-univalent. Apart from the unfamiliar nature of the conception of actually univalent oxygen, it seems natural enough to find a normal molecule of nitric peroxide dissociate at a gentle heat into two identical but simpler ones, in consequence of the linked oxygen atoms becoming parted and losing valency. On the other hand, the assumption that nitrogen is quadrivalent does not accord with the result actually obtained, when by cooling nitric peroxide it is found that the valency of the nitrogen decreases instead of increasing, 2O:N:O becoming O:N:O:N:O .—*Journ. College of Science, Imperial University, Tokyo, xix., Art. 17.*

THE ATOMIC WEIGHT OF TUNGSTEN.*

By EDGAR F. SMITH and FRANZ F. EXNER.

(Concluded from p. 52).

Preparation of Tungsten Hexachloride.

CHLORINE, free from oxygen and moisture, is absolutely essential to obtain this compound pure and in comparatively large amounts. The product must also be sublimed repeatedly in an atmosphere of chlorine, without exposure to the air. The first condition, although apparently simple, is really very difficult to attain; and after much experimenting, we cannot say that we got chlorine absolutely free from moisture. But the quantity of oxychloride formed along with the hexachloride may be taken as an index of the amount of moisture (also oxygen) in the chlorine.

The generator was charged with material sufficient to yield chlorine an entire day without the addition of acid, and consequent introduction of air into the apparatus. When the flow of gas commenced to grow less only the gentlest heat was applied for a few minutes to the generator. The chlorine was most completely dried by conducting it through three six-inch U-tubes, connected in series, containing pumice stone saturated with pure concentrated sulphuric acid, and in the bend sufficient acid to fill the bottom of the tubes, thus causing the gas to bubble through the acid before each new preparation. Indeed, it was about every fourth day that a renewal was made. Only traces of oxychloride were observed. The reaction of chlorine and metal took place in a combustion tube of soft glass, 15 to 18 m.m. in diameter and 4½ feet in length. The tube was contracted in two places to the thickness of a lead pencil, thus making three sections, of which the first was 3 feet in length, the second 1 foot, and the last ½ foot. A porcelain

boat carried the tungsten metal. The chlorine was passed through the apparatus for two hours before any heat was applied. This was done to expel the air. Then the burners of the furnace (to within three of the boat) were lighted, beginning with those most distant from the boat, the flames being small. The tube beyond the boat thus reached a temperature of nearly 350° C. These burners were then extinguished, while those immediately beneath the boat were lighted, the flames being small. The tube to a length of eight inches beyond the boat was also heated. In a very short time the reaction began, noticeable at first in the yellow vapours which condensed in the colder part of the tube, beyond the furnace, to the light brown oxychloride. This did not continue more than two minutes, when copious reddish brown vapours appeared, and condensed beyond the lighted burners to brilliant blue-black needles. The formation is very rapid. The utmost vigilance is constantly required to the very conclusion of the experiment. In two hours 20 grms. of metal may be fully converted into hexachloride. That portion of the combustion tube at which the hexachloride condenses should be kept just hot enough to cause the traces of oxychloride to pass beyond the hexachloride. This can be readily adjusted after a little experience. When working with large amounts the deposits of the hexachloride may obstruct the tube. In that event manipulate a lamp-flame with the hand beneath the chloride until it is partially melted. This converts it into a compact solid, requiring less space. Melting and re-sublimation of the chloride removes every trace of oxychloride. Two sublimations are sufficient for the purpose. The tube can then be sealed off at the contracted points. Perfectly pure hexachloride has a beautiful brilliant steel-blue colour. It can be readily transferred to clean dry weighing bottles, and preserved in them. It has marked stability. There is no perceptible action on bringing the chloride into water at the ordinary temperature, even after considerable time. On the application of heat the decomposition does not begin until the temperature of the water reaches 60°. The specific gravity of the hexachloride, taken in water at the ordinary temperature, equalled 3.518. After all the weighings were made the water employed for the purpose was tested with litmus; it gave the very faintest acid reaction. Having obtained in the above manner large quantities of the hexachloride, it was decided to change it to trioxide, and thus arrive at the atomic weight of the metal. Roscoe had determined the chlorine in this compound. His results were not especially concordant. Perhaps this was due to the involved method or to the presence of traces of oxychloride. However, our thought was to adopt the simplest available course, hence we aimed to convert the chloride into oxide. Roscoe has stated that when hexachloride is directly decomposed with water and the resulting acid ignited to oxide, the latter will contain chlorine which cannot be expelled by heat. We had hoped to pursue this method, but as it had the condemnation of so high an authority the hexachloride was introduced into freshly distilled ammonia water, contained in a weighed platinum dish, with the expectation of eventually getting ammonium tungstate and chloride which would leave the trioxide upon ignition. Experience showed that the quantity of the resulting ammonium chloride was so great that even with the most careful ignition there was much danger of expelling mechanically appreciable amounts of the oxide. Nor was it forgotten that it is very doubtful whether from such a mixture the chlorine could be completely removed by heat.

The treatment of the hexachloride directly with nitric acid was also found impracticable.

In spite of Roscoe's objection to the decomposition with water, it was believed that the transposition could be carried out. Five glazed No. 2 porcelain crucibles of 40 c.c. capacity were selected, thoroughly cleansed and ignited, allowed to cool in vacuum desiccators, and weighed upon a specially constructed Troemner balance, sensitive to one-tentieth of a milligram. There was next introduced into

* From Proceedings of the American Philosophical Society, vol. xliiii., No. 176.

each one of them tungsten hexachloride from a weighing bottle, which was re-weighed after the removal of each portion. The crucibles with their chloride content were placed on water-baths, and cold distilled water introduced into each. When the volume of water was insufficient for the quantity of chloride, sufficient heat was generated by the reaction to make the water boil, and spattering followed. At 60° the decomposition proceeded quietly to the hydrated trioxide, which at the beginning had a slight greenish yellow colour, due probably to imperfect decomposition, as mentioned by Roscoe, but this tint disappeared as the hydrochloric acid was expelled. When the mass was perfectly dry a few drops of pure concentrated nitric acid was introduced from a pipette upon the trioxide. Instantly any green tint vanished, and was replaced by a rich orange-yellow colour. The excess of nitric acid was slowly evaporated away, and the oxide assumed a pale yellow hue.

The crucibles were now removed from the water-bath, and after careful drying were ignited for half-an-hour to a dull red heat, then allowed to cool in the desiccator, and at the expiration of an hour and a-half were weighed.

In the calculations the values for oxygen and chlorine were taken at 16 and 35.45 respectively. The specific gravity of tungsten trioxide was found to be 7.157, and that of tungsten hexachloride 3.518.

Seven different series of determinations were made, each from a different sample of hexachloride. The results appear in the subjoined table:—

No. of expt. series.	No. of of	Weight of WCl ₆ corrected for vacuum. Grms.	Weight of WO ₃ corrected for vacuum. Grms.	Atomic weight of W.	Means of series.	Mean of means.
1.	I.	3.18167	1.86085	184.04	184.01	
2.		2.66612	1.55903	183.94		
3.		3.52632	2.06244	184.05		
4.	II.	1.52117	0.88972	184.07	184.04	
5.		1.22299	0.71523	184.00		
6.		2.28445	1.33603	184.01		
7.		3.25404	1.90337	184.10		
8.	III.	3.37078	1.97133	184.01	183.98	
9.		7.76488	4.54082	183.98		
10.		2.08764	1.22114	184.11		
11.	IV.	2.80141	1.63859	184.09	184.08	184.04
12.		3.24328	1.86681	184.02		
13.		4.97975	2.91262	184.06		
14.		3.04036	1.77838	184.10		
15.	V.	4.31046	2.52133	184.10	184.06	
16.		2.21201	1.29381	184.07		
17.		2.70368	1.58135	184.06		
18.		3.60658	2.10934	184.03		
19.		2.63037	1.53835	184.02		
20.	VI.	3.41668	1.99808	184.07	184.04	
21.		3.49940	2.04675	184.06		
22.		3.86668	2.26145	184.05		
23.		3.40202	1.98970	184.03		
24.	VII.	3.20661	1.87533	184.01	184.06	
25.		3.26386	1.90909	184.09		
26.		6.73833	3.94031	183.94		
27.		7.37889	4.31643	184.14		

It should be mentioned here that at the conclusion of these experiments etching or corrosion of the glaze of the crucibles could not be observed. Nor was there any stain upon them; they looked as if they had been unused.

Metallic Tungsten.

It would be superfluous to set forth here the steps taken in procuring the metal. They are familiar to every reader. They were identical with those described by Hardin. One point, however, is worthy of notice. It was discovered that if the trioxide, reduced to metal, had been previously gotten by the ignition of ammonium paratungstate in vessels of platinum, then it might well be expected that

after the removal of the tungsten from the reduction boats the latter would show dark spots here and there. This occurred, but uncontaminated trioxide was repeatedly reduced in porcelain by hydrogen without leaving dark stains.

Several experimenters—Riche, Desi, Shinn, and Hardin—endeavoured to reach the atomic value of tungsten by collecting the water resulting from the reduction of definite amounts of trioxide in hydrogen. Their results were disappointing in the extreme, although the method is surely rational and in some measure ideal. The reasons for its failure have never been satisfactorily explained. We were induced to give it trial. Every attention to detail was scrupulously observed. The results were most disappointing, and yet we cannot give a reasonable explanation for our failure. There seems to be an inherent defect in the method which we were unable to lay bare.

We also reduced definite quantities of trioxide to metal, and from the loss in weight sought to get the atomic value of tungsten. Again the results were discordant. The boats were never stained from the reduction, nor was the porcelain tube in which the reduction took place stained, but on close scrutiny particles of metal could be seen along the sides of the tube. They rested loosely upon it, and were removed with ease. This metal, in all probability, was carried out into the tube by the aqueous vapour produced in the reduction. This is therefore a serious point in this method.

There remained, finally, only Method 2, another time-honoured method, upon which much discredit had been cast. Yet with pure material it seemed worth the while to give it further trial. The metal used in this study was made from trioxide obtained from the hexachloride. Portions of it were weighed out into the same crucibles which had been used in the experiments with the hexachloride and gently heated with air contact. The steps in the ignition were those which any careful analyst would observe, so that they need not be mentioned here. The final oxide was uniformly yellow in colour throughout its entire mass.

The weighings here, as in all previous experiments, were reduced to vacuum standard. The value of oxygen was placed at 16. The specific gravity of the oxide was, as before, 7.157, and that of the metal—19.

In the appended table it is to be understood that each single series was made from portions of the same sample of metal. The results are:—

No. of expt. series.	No. of of series.	Weight of W. Grms.	Weight of WO ₃ Grms.	Atomic weight of W.	Means of series.	Mean of means.
1.	I.	2.24552	2.83144	183.96	183.96	
2.	II.	1.78151	2.24619	184.07	184.07	
3.	III.	1.63590	2.06270	183.98	184.04	
4.		1.38534	1.74665	184.04		
5.		1.29903	1.63774	184.09		
6.	IV.	2.01302	2.53781	184.12	184.09	
7.		2.18607	2.75632	184.01		
8.		2.36755	2.98478	184.12		
9.		1.94958	2.45781	184.12		
10.	V.	4.43502	5.59141	184.09	184.10	184.065
11.		2.37630	2.99545	184.11		
12.		2.58780	3.26660	184.08		
13.		2.58503	3.25886	184.14		
14.	VI.	2.38298	3.00441	184.06	184.11	
15.		2.03578	2.59169	184.13		
16.		3.60828	4.54915	184.08		
17.	VII.	6.22621	7.84949	184.11	184.12	
18.		5.28444	6.66239	184.08		
19.	VIII.	3.99095	5.03138	184.12	184.12	
20.	IX.	7.30166	9.20647	184.00	184.00	
21.	X.	3.41413	4.33870	184.10	184.08	
22.		2.67709	3.37541	184.01		
23.		4.96735	6.26229	184.13		

In Series VII., a very large quantity of oxide was heated in hydrogen from 9 a.m. until 5 p.m. The resulting metal was placed over night in a desiccator, and on the following day a portion of it was weighed out for the eighteenth experiment, the remainder being heated for a day more in hydrogen. After standing over night a second portion was removed and used in Experiment 19. The remainder was exposed all of the third day to the action of hydrogen, and was then oxidised for Experiment 20. Had not the first reduction been complete, the results would not have agreed so well.

The mean atomic value from the hexachloride is 184.04, that from the oxidation of metal 184.065, or the average of the two independent series is 184.05, which probably approximates the truth very closely, and may be safely regarded as the atomic weight of tungsten.

Summary.

Our study, extended over so long a period, has revealed:—

1. That it is quite doubtful whether any chemists who in the past occupied themselves with a determination of the atomic weight of tungsten have worked with pure substance. Tungstic acid is prone to form "complexes." It was found that if the acid contain no iron, for instance, but be digested with acids, e.g., hydrochloric or nitric acid, in which iron is present, the latter will enter the tungstic acid. Iron and manganese are eliminated from the acid with the greatest difficulty. In the earlier work there is no evidence of their removal. Neither do we discover that vanadium and phosphorus had been considered as present, yet in purifying ammonium paratungstate by re-crystallisation alone it was found that the tenth re-crystallisation showed vanadium.

2. The slimy greenish or bluish white masses, believed to be "paratungstates" because of their great insolubility, are probably "complexes."

3. The fourth method of purification can be relied upon to yield pure tungstic acid.

4. The use of pure sodium carbonate (2 per cent) to dissolve tungsten trioxide gives an excellent means of ascertaining when the iron, manganese, and silica are fully removed, but that its development into a method for the determination of the atomic weight of tungsten is not at all probable.

5. The plan of digesting pure ammonium paratungstate with nitric acid, then evaporating to complete dryness and gently igniting, affords pure oxide.

6. That porcelain vessels are preferable to those of gold, silver, or platinum for the ignition of ammonium paratungstate and tungstic acid.

7. That the oxidation of metal (Method 2) leads to reliable atomic numbers when the material is pure.

8. That tungsten hexachloride can be completely transposed into pure oxide with water and a little nitric acid.

considering it to be gum. Professor Wiesner (Abstract, *Pharmaceutical Journal*, 1871, Series 3, vol. ii.) stated that it was closely allied to Acacia gum, and J. H. Maiden (*Proc. Linn. Soc. N.S.W.*, 1899 and 1891) later formed one of his *Eucalyptus* kino groups (the Gummy Group) upon its presence. It does not appear possible to obtain it in a crystallised condition, nor could it be removed from aqueous solution by miscible solvents. It was obtained in as pure a condition as possible by repeated precipitation by alcohol from concentrated aqueous solutions. When dried and powdered, it was of a cinnamon colour, and this colour was not removed by boiling with animal charcoal. It is very soluble in water, and when boiled with acid for some time a "kino red" is formed in quantity, a sugar being separated at the same time. The "kino red" dyes mordanted cloth a series of browns, alumina giving the best colour. When fused with potash it forms protocatechuic acid, but not phloroglucinol. The sugar had no rotation, was reduced by Fehling's solution readily, was slowly but entirely fermented by yeast, and gave an osazone soluble in hot water, and which melted at 176—178° C. Were it not that it was inactive to light it might, from these reactions, be supposed to be melibiose, which is formed from melitose (*Eucalyptus* sugar) by hydrolysis, levulose being split off at the same time, This glucoside, for which the author proposes the name *Emphloin* (as it principally occurs in the bark of certain species), is found in almost a pure condition in those *Eucalypts* known as "Ironbarks." The kinos of the "Stringybarks" and of the "Peppermints," although consisting of the same tannin, do not contain sugar and are not glucosides, but the author has already isolated glucoside, *Myrticolarin*, from the "Stringybarks," the sugar of which is glucose. This kino glucoside is practically a bark product, occurring in species which do not appear to give *Eucalyptus* Manna. Melitose, however, is found in the bark of certain species in which the tannin is principally located in the wood, as in *E. punctata*. For these reasons the author thinks that melitose itself should be considered a glucoside, the third glucose molecule taking the place of the tannin in the glucoside. The quantitative results and the relative astringent values show the substance to contain an equivalent to two glucose molecules. Although entirely precipitated by gelatin, the glucoside has very slow action on hide, and thus the sluggishness of "Ironbark" liquors is accounted for. It now remains to devise a method whereby the glucoside may be cheaply hydrolysed, and thus the tannin in the bark of *E. sideroxyloides*, for instance, be made available for tanning purposes.

NOTICES OF BOOKS

Introduction to Physical Chemistry. By JAMES WALKER, D.Sc., F.R.S., &c. Third Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1903. Pp. 368.

MODERN science tends more and more to bring together what were at one time looked upon as two separate sciences, viz., Chemistry and Physics, the result being now known as "Physical Chemistry." These is still, however, a strong tendency on the part of the student to keep his every-day chemistry and his physical chemistry apart. This is brought about to a great extent by the general methods of teaching adopted, by which what we may term the old chemistry is first drilled in, to be followed a few years after by the new ideas which seem only to complicate matters.

In this volume the author has endeavoured to smooth away the difficulties which beset the young student, and to bring out as clearly as possible the actual connection between the old and the new science, or perhaps more correctly to show how the latter has developed naturally from the former.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES.

THE General Monthly Meeting of the Society was held at the Society's House, No. 5, Elizabeth Street North, on Wednesday evening, June 1st, 1904; C. O. BURGE, M. Inst. C.E., President, in the chair.

"On the Absence of Gum, and the Presence of a New Diglucoide in the Kinos of the *Eucalypts*," by HENRY G. SMITH, F.C.S., Assistant Curator, Technological Museum.

In this paper, which is the first of a series dealing with *Eucalyptus* kinos, the author shows that the supposed gum occurring in many *Eucalyptus* kinos is not gum but a peculiar tannin diglucoide. The insolubility in alcohol of this substance seems to have been the only reason for

The present edition differs from those that have preceded it in many points of detail. Newer data and more accurate numerical determinations have been adopted wherever available, and an additional chapter (Chapter XXVII.) has been written on electromotive force, while Chapter XXVIII., on thermodynamical proofs, dealing with the same subject, has been extended.

The book has been brought up to date as far as possible, and will no doubt attain as great success as the former editions.

A Method for the Identification of Pure Organic Compounds. By SAMUEL PARSONS MULLIKEN, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

THIS large volume represents an attempt at simplifying the labour of identifying organic compounds by giving systematised information concerning all known substances, classified together according to their behaviour when subjected to certain specified tests. Hitherto, when an investigator in the course of research has prepared a substance unfamiliar to him, in order to identify it he has been obliged to find its percentage composition and molecular weight, and then compare its properties with those of other compounds of the same empirical formula, which often entails consulting a large number of authorities, and is at the best a tedious and laborious process. The author of this work has devised a method of classification first of all into what he calls orders, *i.e.*, classes comprising compounds containing the same elements, then into genera, characterised by their behaviour on the application of certain chemical tests, and the various members of each genus are then tabulated according to the value of some readily determined physical constant, such as the melting- or boiling-points; various other characteristics of each member of the genus are also specified, and simple corroborative tests appended, so that the investigator should finally be able to be absolutely certain of the identity of his unknown substance, and that with comparatively little trouble. In the examples given of actual experiments performed, two typical though perhaps rather easy specimens were identified in one hour fifty minutes and two hours fifty-five minutes respectively, 0.8 gm. of the substance being consumed in each case. This speaks for itself when we consider the time that would probably be occupied in identifying an unknown substance by the old method, and, moreover, no account is taken of the fact that the investigator would probably have some clue as to the genus of his compound, which might shorten the labour considerably.

The collection of data concerning 2300 substances has, of course, involved an enormous amount of work, but exceeding conciseness and the judicious use of abbreviations have kept the book quite within the limits of ordinary size. This first part contains only the compounds of carbon with hydrogen, and with hydrogen and oxygen, and practically all such compounds are included excepting some uncrystallisable syrups which cannot be distilled without undergoing decomposition, the oily and fatty glycerides, and some glucosides and sugars, specimens of which could not be obtained for analysis. A second volume containing compounds of carbon with nitrogen, and nitrogen and oxygen, and a third to include the compounds of carbon with the other more important elements, are to be issued, and will, no doubt, with this be acceptable to the somewhat limited circle of readers to whom such works can appeal.

Jahrbuch der Elektrochemie. IX. Jahrgang. ("Electrochemical Annual." Vol. IX.). Edited by Dr. HEINRICH DANNEEL. Halle-a-S.: Wilhelm Knapp. 1904.

THIS volume, which contains the reports for the year 1902, has only just appeared, which greatly diminishes its value as an annual. As in preceding years, in it is discussed the progress which has been made during the year, both in

pure and applied electrochemistry, and improvements in apparatus and manufacturing processes are also fully described. It also contains the contributions which have been made to our knowledge of the theoretical aspects of the science, and a somewhat belated book review, chiefly relating to books which have appeared in Germany, though one American work receives rather a grudging notice. A vast amount of useful information is contained in the volume, which can lay claim to being comprehensive, and a full account of almost any point connected with electrochemistry could be obtained by looking it up in this book, for the leading current periodicals have been carefully searched and articles of interest and importance abstracted.

Atti della Società Elvetica di Scienze Naturali. ("Transactions of the Swiss Scientific Society"). Zürich: Zürcher and Furrer. 1904.

THIS volume contains the programme of the meetings of the Swiss Scientific Society, which held its eighty-sixth session at Lucerne in September, 1903, together with verbatim reports, either in German, French, or Italian, of the papers read before the general assembly; detailed accounts are given, in some cases copiously illustrated, of the commissions appointed to examine various questions of scientific interest, and also the reports of the auxiliary biological, geological, and chemical societies; these latter are sufficient to give an interesting insight into the workings and activity of a society which appears to combine in itself the vigour of youth with the stability of age. The biological sections in particular appear to be specially flourishing, and most of the papers and communications relate to this branch of natural science. The volume closes with biographical obituary notices of the members who have died in the years 1902 and 1903.

CORRESPONDENCE.

PEROXYLAMINESULPHONIC ACID.

To the Editor of the Chemical News.

SIR,—Permit me to point out a mistake in the first line of my paper on "Peroxylaminesulphonic Acid" (CHEMICAL NEWS, vol. xc., p. 42), which runs—"Although unrecorded in works on . . . chemical technology . . ." As a matter of fact, mention of the production of a violet colour in the acid in the Gay-Lussac tower is to be found in all three editions of Lunge's "Sulphuric Acid and Alkali." The treatment of the subject discussed in the paper is in no way affected by this statement in error; but, in correcting it, I desire to express my regret at having made it. At the time of writing the paper I was unable to make adequate references, and therefore invoked the aid of a most competent but busy friend in looking-up the matter for me, and he wrote that he could find nothing about the subject in Lunge's treatise. Professor Lunge has been good enough to inform me that he has also published an account of an investigation of the nature of this blue or purple colour in *Dingler's Journal* and in the *Berichte* in 1879. The colouration had already been noticed by C. Winkler and R. Weber. But Lunge ascertained that the production of the colour is due to interaction between sulphur dioxide, mercury (or other reducing agent), and nitrososulphuric acid, so far anticipating Sabatier's observations.—I am, &c.

EDWARD DIVERS.

Synthesis of Pentamethylene Glycol, $\text{HO}(\text{CH}_2)_5\text{OH}$, of Nitrile, and Pimelic Acid.—J. L. Hammett.—To obtain pentamethylene glycol the author transforms the dibromopentane into diacetate, and this, by saponification, into glycol.—*Comptes Rendus*, cxxxiv., No. 1.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxiv., No. 1, July 4, 1904.

Synthesis in the Anthracene Series. Dihydride of γ -Triphenylanthracene and Derivatives.—A. Haller and A. Guyot.—In a former research the authors described the preparation and chief properties of symmetric γ -diphenylanthracene dihydride and a few of its derivatives. They now continue their experiments, and describe the triphenyl derivatives and the conditions under which they are prepared. Theoretically they should be produced in several ways. These different methods are described in detail and the products obtained in each case.

Determination of the Atomic Weight of Nitrogen by Analysis by Volume of Nitrogen Protoxide.—Adrien Jaquero and M. St. Bogdan.—The authors determine the atomic weight of nitrogen by the volumetric analysis of one of the oxides of nitrogen. The method consists in decomposing nitrogen protoxide in an hermetically sealed tube by means of an iron wire heated by the electric current. The oxygen unites with the iron, leaving pure nitrogen. The weight deduced is 14.019 as the mean of all the experiments.

Allotropic Forms of Antimony Sulphide. Heat of Formation.—M. Guinchant and Chrétién.—The authors succeed in isolating a modification of antimony sulphide in a pure state; this is the stable form at a high temperature. The heat of formation is less than that of the black sulphide, the stable form at a low temperature. They also determine the heat of transformation of the different allotropic modifications of antimony sulphide when these pass to the stable form, admitting Berthelot's value for wet precipitated sulphide:—

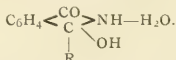
$\text{Sb}_2 + \text{S}_3 \text{ oct.} + \text{H}_2\text{O} = \text{Sb}_2\text{S}_3 \text{ wet precipitate} \dots + 34.0 \text{ cal.}$
 From this the following numbers are deduced for 1 mol. or 336 grms.:—

$\text{Sb} + \text{S}_3 \text{ oct.} = \text{Sb}_2\text{S}_3 \text{ dry precipitate} \dots + 32.6 \text{ cal.}$

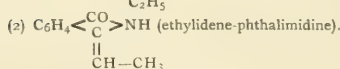
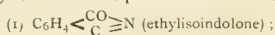
$\text{Sb}_2 + \text{S}_3 \text{ oct.} = \text{Sb}_2\text{S}_3 \text{ lilac precipitate} \dots + 33.9 \text{ cal.}$

$\text{Sb}_2 + \text{S}_3 \text{ oct.} = \text{Sb}_2\text{S}_3 \text{ black precipitate} \dots + 38.2 \text{ cal.}$

Action of Mixed Organo-magnesium Compounds on Phthalimide and Phenylphthalimide.—Constantin Béis.—In a preceding research the author showed that M. Grignard's mixed organo-magnesium compounds react on phthalimide, and that the products of this reaction, when treated with water, are decomposed into a body corresponding to—



This dehydration can take place in one of two ways:—



The author's experiments lead him to believe the latter to be the correct formula.

Action of Ammonia Gas on Arsenic Trichloride, Tribromide, and Triiodide.—C. Hugot.—Ammonia gas reacts at a low temperature on trichloride, tribromide, and triiodide of arsenic, giving arsenic amide. A chloride, bromide, or iodide of ammonium is formed at the same

time, according to the arsenic compound used. The amide thus prepared can be used to form also the imide and nitride of arsenic.

A Method of Decomposing the Lactic Acid of Fermentation into its Components Active to Polarised Light.—E. Jungfleisch.—The author describes a method of decomposing the lactic acid produced during fermentation into its active components. This method is founded on the difference in properties between *d*-lactate, *l*-lactate, and (*d*+*l*) lactate of quinine.

Iodine Compounds obtained with Metanitrilaniline.—P. Brenans.—The author prepares the following iodine compounds from metanitrilaniline:—(1) Di-iodonitrilaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_4\text{I}_2 = \text{NO}_2 \cdot 1.2.6.3$; (2) di-iodonitrobenzene, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 = \text{I}_2 \cdot 1.2.4$; (3) di-iodoaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 = \text{I}_2 \cdot 1.2.4$; (4) Di-iodophenol, $\text{OH} \cdot \text{C}_6\text{H}_3 = \text{I}_2 \cdot 1.2.4$.

New Synthesis of α -Dimethyladipic Acid.—G. Blanc.—The author has previously shown that when $\text{C}_2\text{H}_5\text{O} \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$, α -dimethylsuccinic ether,

is reduced by sodium and alcohol, a lactone, $\text{C}_6\text{H}_{10}\text{O}_2$, is formed besides the glycol. This lactone, when treated with potassium cyanide, gives α -dimethylglutaric acid by hydrolysis of the product of the reaction. The same method may be applied to dimethylglutaric ether, the resulting product being α -dimethyladipic acid.

Atmospheric Formaldehyde.—H. Henriet.—The author discovers an important objection to the accuracy of his former estimation of atmospheric formaldehyde, owing to the existence in the air of a compound of this aldehyde. He is continuing his researches on this question.

Bulletin de la Société Chimique de Paris.
 Series 3, vol. xxxi., No. 2.

Action of Isocyanate of Phenyl on some Univalent Alcohols. (II.)—A. Bloch.—The author easily obtained cholesterylphenylurethane by heating anhydrous cholesterol to 180° with isocyanate of phenyl. The net return was 70 per cent. With sulphuric acid it gives a bright orange-yellow colouration, becoming brown after fifteen or twenty minutes. When heated in a test-tube it decomposes and forms a white sublimate. Heated in the air it commences to decompose at about 280° , giving off carbonic acid slowly and regularly, till there finally remains a brown fluorescent liquid mass containing aniline, while on the sides of the tube there is a slight deposit of diphenylurea.

Action of the Diazo Chlorides in Excess in Alkaline Solution on Oxalacetic Ether.—J. Rabischong. Two-tenths of a molecule of aniline are dissolved in 50 c.c. of hydrochloric acid at 40 per cent, and treated with 100 c.c. of water. It is diazotised at 0° with two-tenths of a molecule of nitrite of soda and kept at this temperature. At the same time a tenth of a molecule of oxalacetate of ethyl, or 18.8 grms., is treated with 100 c.c. of a solution of soda of such strength as to saturate exactly the 50 c.c. of hydrochloric acid added to the aniline. This latter solution is cooled and the chloride of diazobenzene poured in very slowly. Gas is given off, and gradually a very thick, deep-red body is formed. The reaction continues for several hours, and the liquid takes the form of a soft mass. The substance is purified by two recrystallisations in absolute alcohol. Analysis gives it the formula of diphenylformazylformate of ethyl.

Action of the Diazo Chlorides on the Oxalacetic Ethers.—J. Rabischong.—A tenth of a molecule of aniline, or 9.3 grms., is dissolved in 25 c.c. of pure hydrochloric acid at 40 per cent, and treated with 50 c.c. of distilled water. This solution, cooled to 0° , is diazotised by a tenth of a molecule, or 6.9 grms. of nitrite of soda dissolved in 100 c.c. of water also cooled to 0° . At the same

the other, a brown salt, is altogether different, $(\text{S}_2\text{O}_3)_2\text{BiRb}_2\text{H}_2\text{O}$. The yellow salt is obtained in a similar manner to the potassium salt. The brown salt is formed by treating the yellow salt with a quantity of water insufficient to dissolve it. The two salts become anhydrous over P_2O_5 . The caesium salt, which is anhydrous, $(\text{S}_2\text{O}_3)_2\text{BiCs}$, is obtained by precipitating a nitric solution of nitrate of bismuth, nitrate of caesium, and hyposulphite of soda with alcohol. It is more stable than the salts of potassium and rubidium. The barium salt, $[(\text{S}_2\text{O}_3)_2\text{Bi}_2]\text{Ba}$, is obtained by the double decomposition of an alcoholic solution of a sodium salt and a solution of BaCl_2 ; the precipitate is pale yellow, and is strongly hydrolysable on contact with water; the solution deposits a basic salt. This compound, when pure, is fairly stable; when moist it decomposes rapidly into sulphide of bismuth and sulphate of barium.—*Zeit. Anorg. Chem.*, vol. xxxv., p. 1.

Pure Rhodium.—S. M. Jorgensen.—This metal is obtained by the reduction of the chloride $\text{Cl}(\text{Rh}_3\text{NH}_3)_2\text{Cl}_2$ by means of hydrogen. This chloride, prepared according to the method already described by the author (*Journ. f. Prakt. Chem.*, [2], vol. xxvii., p. 435), is not chemically pure, but contains a little iridium. The purification is easily effected by dissolving 10 grms. of the salt in 250 c.c. of NO_3H ($D = 1.40$), and heating on the water-bath until a small quantity diluted with water does not become cloudy with nitrate of silver. On cooling, we obtain the chloropentammonium nitrate. Dilute with its own volume of water, filter, and wash with NO_3H (1 vol. of acid, $D = 1.4 + 2$ vols. of water), then with alcohol. The salt obtained is dissolved in water and filtered, and the filtrate is collected in concentrated hydrochloric acid. The precipitated chloride, washed with dilute hydrochloric acid, then with alcohol after a second treatment with nitric acid, is dissolved in dilute soda and then precipitated by boiling with hydrochloric acid. Dissolve in boiling water and precipitate again with hydrochloric acid. After three dissolutions and re-precipitations the precipitate is free from soda and from HNO_3 .—*Zeit. Anorg. Chem.*, vol. xxxiv., p. 82.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volume Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

176, NEWCASTLE ST., FARRINGTON ST., E.C.

IMPERIAL COLLEGE OF CHEMISTRY, 49 & 51, IMPERIAL BUILDINGS LUDGATE CIRCUS, E.C.

Principal—FREDERICK DAVIS.

PRACTICAL AND THEORETICAL TUITION

in Botany, Chemistry, Pharmacology, and Therapeutics for All Medical and Science Examinations.

General Course of Instruction in Therapeutics, Pharmacology, and Microscopy for Institution of Chemistry Exam.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC, As described in the "Report of the Island Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, SHOT, &c.

RADIUM

(BROM PUR.)

FROM STOCK

in

1, 2, & 5 m.g.

Tubes.



ON HIRE,

or at

REASONABLE

PRICES.

Pitchblende, from 2/- to 30/- per piece; in Powder, 2/6 per oz.
Kunzite, selected, 2/- per gramme. Carnotite, 2/- per oz.
Aeschynite, 2/- per oz.
Spartite (see NATURE, March 31, 1904, page 523), 2/- per piece.
Chlorophane, 2/- per piece. Samarskite, 2/- per oz.
Zinc Sulphide, green and yellow, 2/6 per tube.
Rad. Residue, 2/- per tube. Polonium, 21/- per gram; 11/- 1/2 gram.
Polonium on Bi. rod, 25/- Willemite, 2/- per oz.
Flexible Sandstone, 3/- to 50/- (See NATURE, June 23, 1904, page 185)
Monazit, 3/- per oz. Monazit Sand, 1/- per oz.
Diamond chips and powder, 10/- per carat (best quality).
Euklas, Hidentit, Wagnerit, Phosgenit.
Bar. Plat. Cyan., for Screens, 3/- gramme, 60/- oz. Crystals, 4/- gramme. Screens, 9d. per square inch.
Radio-active Screens, 6d. per square inch. Willemite Screens 6d. per square inch. Electrosopes (special), 21/-.
Sinthariscopes (special), 21/-, 10/6 and 7/6.
Selection of Minerals in Boxes, 2/6, 5/6, 10/6 and 21/-.

NEW ZEALAND VEGETABLE CATERPILLAR; from 2 to inches long, with a stem showing fructification growing out of its head. Specimens may be had from 10/6 to 21/-, according to quality and size.

See NATURE, May 12, 1904, page 44.

Goods may be returned if not approved of, when money will be refunded. Professional Men, Universities, Schools, &c., allowed special terms.

ARMBRECHT, NELSON & CO.

71 & 73, Duke St., Grosvenor Square, W

UNIVERSITY OF BIRMINGHAM.

Faculties. —

SCIENCE.
ARTS.

MEDICINE.
COMMERCE.

SPECIAL SCHOOL OF MODERN LANGUAGES.

DEPARTMENT FOR TRAINING OF TEACHERS

Schools of

ENGINEERING,
METALLURGY.

MINING,
BREWING.

DENTISTRY.

Leading to Degrees and Diplomas.

The Session 1904-5 commences October 3rd, 1904.

ALL COURSES AND DEGREES ARE OPEN TO BOTH MEN AND WOMEN STUDENTS.

In the Medical School there is a separate Dissecting Room for Women, with a qualified Woman Demonstrator.

Graduates of other Universities may, after two years' study or research, take a Master's degree

SYLLABUSES with all information will be sent on application to the Secretary.

THE

DURHAM COLLEGE OF SCIENCE

NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided

for Students of both sexes proceeding to the University Degrees in Science, or in Letters, and for the University Diploma in Theory and Practice of Teaching. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 26th. Lectures begin October 4th, 1904.

Prospectuses on application to the SECRETARY.

THE CHEMICAL NEWS.

VOL. XC., No. 2333.

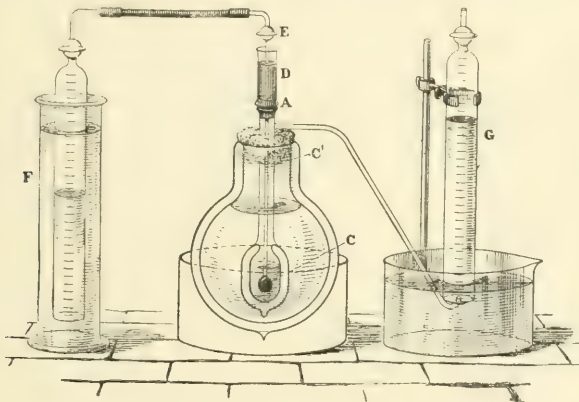
THE ABSORPTION AND THERMAL EVOLUTION OF GASES OCCLUDED IN CHARCOAL AT LOW TEMPERATURES.*

By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S.,
Jacksonian Professor, University of Cambridge, and Fellenius,
Royal Institution, London.

DURING the year 1874-5, in association with the late Professor Tait, a research was undertaken which involved the production of very perfect vacua, and with the object of improving on the then known methods, dense charcoal was employed as an efficient absorbent of traces of any gaseous residuum.

An account of these experiments communicated to the Royal Society of Edinburgh appeared in *Nature*, July 15, 1875, under the title of "Charcoal Vacua."

In Professor Clerk Maxwell's Notes on "Molecular Physics" the following succinct description of the process is given:—



"Another method employed by Professor Dewar is to place in a compartment of the vessel a piece of freshly heated cocoanut charcoal, and to heat it strongly during the last stages of the exhaustion by the mercury pump. The vessel is then sealed up, and as the charcoal cools it absorbs a very large proportion of the gases remaining in the vessel.

"The interior of the vessel, after exhaustion, is found to be possessed of very remarkable properties.

"One of these properties furnishes a convenient test of the completeness of the exhaustion. The vessel is provided with two metallic electrodes, the ends of which within the vessel are within a quarter of an inch of each other. When the vessel contains air at the ordinary pressure a considerable electromotive force is required to produce an electric discharge across this interval. As the exhaustion proceeds, the resistance to the discharge diminishes till the pressure is reduced to that of about a millimetre of mercury. When, however, the exhaustion is made very perfect, the discharge cannot be made to take

place between the electrodes within the vessel, and the spark actually passes through several inches of air outside the vessel before it will leap the small interval in the empty vessel. A vacuum, therefore, is a stronger insulator of electricity than any other medium."

At one of the conferences held in connection with the Special Loan Collection of Scientific Apparatus (see "Science Conferences," "Physics and Mechanics," p. 154) in the year 1876, I showed that with a vapour like bromine the absorptive power of the charcoal was so effective that a space filled with the vapour even at atmospheric pressure could be made into a fairly high vacuum showing very wide striae.

When the charcoal was heated the bromine vapour was again expelled, and on allowing it to cool, all stages in the appearance of the electric discharge as the vacuum is reached could be conveniently observed without the use of any form of air-pump.

When in the course of low temperature investigations the perfection of the vacuum vessels for the storage and manipulation of liquid air and hydrogen came to be important, the effect of charcoal on heat isolation in such utensils was fully investigated and confirmed in a paper entitled "Liquid Air as an Analytic Agent" (*Roy. Inst. Proc.*, 1898). Still no systematic experiments on the absorptive power of charcoal at low temperatures were made either at this time or subsequently.

It is the object of the present preliminary paper to contribute some definite quantitative data regarding gas absorption and thermal evolution in charcoal at the temperature of liquid air. The mode in which liquid gases like oxygen or air could be used as calorimetric agents was described in my paper on the "Scientific Uses of Liquid Air" (*Roy. Inst. Proc.*, 1894).

The apparatus was further improved into the form illustrated and described in Madame Curie's work, "Recherches sur les Substances Radio Actives," 2nd edition, p. 100, as used for the determination of the heat evolved by radium bromide either in liquid oxygen or hydrogen. Such calorimeters are easily adapted to the simultaneous observation of the volume of any gas absorbed by charcoal, and of the concomitant heat evolution.

For this purpose a small glass bulb, c, containing from 0.5-1 gram. of charcoal, has a long narrow tube, c', attached, so that it can be immersed in the liquid oxygen or air in the calorimeter, a b, while still allowing a part of the tube to project above the cork a. In order to dry and cool the 40 c.c. of gas, which represents the largest volume

* A Paper read before the Royal Society, June 16, 1904.

taken in by the charcoal in my experiments, a little annular space is arranged at D into which liquid air is poured immediately before the experiment is made.

The charcoal, after being placed in the tube, C, is heated to a low red heat and simultaneously exhausted by a good air-pump, and after all the gas has been removed the stopcock E is closed. In this condition it is placed in the calorimeter.

The experiment is conducted by connecting the end of the tube at E by means of an india-rubber tube with a graduated vessel, F, containing the gas. When all is ready the stopcock E is opened, so that the gas may rush into the charcoal, and the heat evolved by its absorption distils off the equivalent quantity of liquid air from the calorimeter, which is measured in the vessel G.

The constant of the calorimeter being known (which with liquid air is about 14.5 c.c. per calorie), we get the actual thermal evolution together with the volume of gas absorbed.

The heat correction for the rush of gas into the same exhausted glass bulb without charcoal is small in proportion to the total heat evolved, and the same may be said of the volume correction on account of the cooling of the space external to the charcoal. With a variable material like coconut charcoal, I have in the calorimetric experiments used the same sample in all cases. The following table embodies the general results per cubic centimetre of charcoal. The gas absorption is given at 0° and 760 m.m. If the volume of gas absorbed had been measured under the same conditions of pressure at -185° C., then the numbers in Column II. would all have to be divided by three.

	I. Volume absorbed. 0° C. C.c.	II. Volume absorbed. -185° C. C.c.	III. Heat evolved. Grm.-calories.
Hydrogen	4	135	9.3
Nitrogen	15	155	25.5
Oxygen	18	230	34.0
Argon	12	175	25.0
Helium	2	15	2.0
Electrolytic gas	12	150	17.0
Carbonic oxide and oxygen	30	195	34.5
Carbonic oxide	21	190	27.5

In all cases, it will be observed, the amount of gas occluded has been greatly increased at the low temperature, and the degree of condensation is generally such as we should anticipate from the known physical constants of the gases. The amount of heat evolved is so great as to be in excess of that required for liquefaction in the case of gases like hydrogen, nitrogen, and oxygen. The heat produced when successive fractions of the volume of gas required for saturation are absorbed has yet to be determined. In the time required for the absorption no measurable amount of chemical combination was effected between mixtures of hydrogen and oxygen or carbonic oxide and oxygen in the pores of the charcoal.

Such experiments must be extended to the use of platinised charcoal and other catalytic agents.

Perhaps the most striking result is the great difference in properties exhibited by helium. While resembling the other gases in showing increased absorption at the temperature of liquid air the absolute amount occluded per unit volume of charcoal is about one-tenth that of the other gases at the same temperature. There can be little doubt that when the relative absorption of helium in charcoal is measured at the temperature of liquid hydrogen, the increased absorption will be so marked as to make it comparable to that of hydrogen in the present set of experiments. In this case charcoal at the boiling-point of hydrogen will become an efficient condensing agent for helium, and this property will have important applications in future research.

Separation of Highly Concentrated Oxygen from Air.

In order to examine the changes taking place in a mixed gas like air during the absorption, a quantity of about 50 grms. of charcoal was, after heating and exhaustion, saturated at -185° in a current of pure dry air; got by passing the air current through a U-tube immersed in liquid air.

For a time the air rushed into the charcoal with great rapidity, and in about ten minutes between 5 and 6 litres were taken in. A manometer attached to the vessel containing the charcoal showed, on shutting off the air current, that during the early part of the saturation the absorption was so effective as to give practically no measurable mercury pressure. As soon as the absorption was ended, and a current began to pass slowly over the charcoal, the composition of the air leaving the charcoal showed 98 per cent nitrogen. After the current of air had passed for half an hour, the total gas occluded in the charcoal was expelled by taking the vessel in which it had been treated out of the liquid air, and allowing the temperature to rise to 15° C.

The gas, which was rapidly expelled, measured 5.7 litres, and contained 56 per cent of oxygen. If the saturated charcoal before heating up was subjected for an hour to the action of an air-pump, capable of giving a steady exhaustion of 5 m.m., no difference was effected in the oxygen percentage of the evolved gas. The same experiment was repeated with this variation, that, instead of the air current having the pressure of the atmosphere, it was kept below one-tenth of an atmosphere. In this experiment 4.8 litres were expelled on heating up, and the percentage of oxygen was 58. Then a further repetition was made with an air current supplied at a pressure not exceeding 5 m.m. of mercury. After three hours' treatment the charcoal, on heating to 15° C., gave 44 litres of 57 per cent oxygen. From these experiments it follows that the tension of the occluded gases, at the temperature of liquid air, must be very small, and thus the use of low temperatures, combined with charcoal, introduces a new and greatly improved means of getting high vacua, which in the future may be found susceptible of important practical applications. These experiments are quite conclusive as to the practical constancy of the mean composition of the air gases occluded in the charcoal (subject to the conditions aforesaid), and they further show that wide changes in the pressure of the air current has little or no effect in altering the proportions. In another experiment, the vessel containing the saturated charcoal, instead of being allowed to rise rapidly in temperature, was transferred to a vacuum vessel, in which a little liquid air was placed, in order that the temperature might rise slowly, and thereby enable the successive litres of gas given off to be collected separately and analysed.

This experiment gave the following results:—

	Oxygen, per cent.
First litre	18.5
Second litre	30.6
Third litre	53.0
Fourth litre	72.0
Fifth litre	79.0
Sixth litre	84.0

The mean composition of the 6 litres is again 56 per cent oxygen. From the above experiments it follows that one of the most rapid means of extracting a high percentage of oxygen from atmospheric air is to absorb it in charcoal at low temperatures, and then to expel it either rapidly or slowly by heating the mass of charcoal to the ordinary temperature.

A few experiments have been made, using, instead of air, special mixtures of oxygen and nitrogen. Thus it was found that a gas containing 6.5 per cent of oxygen used in the same manner as in the air occlusion experiments gave, on heating up the charcoal rapidly to 15° C., 5 litres of gas having the composition of 23 per cent of oxygen. A

repetition of the same process with the 23 per cent of oxygen would have raised the percentage about 60 per cent, or a stronger concentration could have been reached by fractionating the gas as it slowly leaves the charcoal on gradually increasing the temperature.

This preliminary investigation suggests many fields for further inquiry, and some of these I hope to deal with in future papers.

I have to express my thanks to Mr. Robert Lennox, F.C.S., for efficient aid in the conduct of the experiments, and Mr. J. W. Heath, F.C.S., has also rendered valuable assistance.

A REVISION OF THE ATOMIC WEIGHT OF BERYLLIUM.*

By CHARLES LATHROP PARSONS.

(Concluded from p. 64).

II. Determinations of the Atomic Weight.

SINCE the last investigation of the atomic weight of beryllium was made by Krüss and Moraht, in 1890, two new anhydrous compounds of beryllium have been discovered which are especially fitted for a re-determination of this constant, viz., the acetylacetonate and the basic acetate. The first has the disadvantage common to all compounds previously used, in that it contains a small per cent of beryllium, slightly less than the sulphate, in fact, and any variation in the per cent of beryllium oxide is doubled in the atomic weight. The basic acetate fortunately contains a much larger proportion of beryllium, and in this respect approaches to the composition of the chloride. Both are readily crystallised and sublimed, and lend themselves to a very complete separation of the element from others, which might interfere in the determination. The basic acetate, a compound with very unusual properties and peculiar to beryllium alone, would seem to be especially adapted for this purpose.

The Properties and Analysis of Beryllium Acetylacetonate.

Properties.—Beryllium acetylacetonate was first prepared by Combes (*Comptes Rendus*, cxix., 1221), the discoverer of acetylacetonate itself (*Ibid.*, ciii., 814), and many of the interesting metallic derivatives of that compound. It is most readily prepared by the action of beryllium carbonate or hydroxide on acetylacetonate. It is a perfectly white crystalline substance which is slightly soluble in cold water, more soluble in hot water, and slowly decomposed by boiling water with loss of acetylacetonate and precipitation of beryllium hydroxide. It is readily soluble in alcohol, and is easily crystallised therefrom in rhombic plates, differing widely from the crystals of the corresponding aluminum salt. It is soluble in benzene, toluene, xylene, naphtha, and all petroleum distillates, coloriform, turpentine, methyl alcohol, amyl alcohol, ether, ethyl acetate, acetone, carbon disulphide, and all other solvents at my disposal. It melts at 108°, and boils at 270° without decomposition (Combes, *Comptes Rendus*, cxix., 1222). It sublimed readily many degrees below its boiling-point, and begins to sublime even below the boiling-point of water. The sublimed crystals are light and flocculent, with a marked resemblance to flakes of snow. It is soluble in acids, setting free acetylacetonate.

Preparation of Material.—Two separate lots of material were prepared for the atomic weight determinations.

1. Basic beryllium carbonate, prepared as before described from beryl, was carefully washed with ammonia-free water until absolutely free from sulphates, and while still moist was treated with Kahlbaum's acetylacetonate, which was first re-distilled. Carbon dioxide was slowly evolved, and the insoluble beryllium acetylacetonate left

behind. This was pulverised and washed with pure water to remove excess of acetylacetonate, and was then dissolved in re-distilled absolute alcohol, and filtered to remove any unchanged carbonate. On partial evaporation, beryllium acetylacetonate was deposited. The clear plate-like crystals showed no colour, but were again pulverised, washed with water, dissolved in absolute alcohol, and re-crystallised. This operation was repeated for the third time, and the mother-liquors each time rejected. The crystals so produced were absolutely free from iron, and not the slightest residue of aluminum chloride could be obtained by Havens' method of separation (*Zeit. Anorg. Chem.*, xvi., 15—18). They were pulverised and dried for several hours in an air-bath. After drying they were introduced into a Jena glass retort, connected with a receiver of the same material, and were sublimed in a current of dry carbon dioxide many degrees below their boiling-point. The retort was heated evenly on a bath of rosin kept at 230°, and the neck of the receiver was covered with a piece of silk bolting-cloth, which allowed only the carbon dioxide to pass. The perfectly white light and feathery acetylacetonate was again introduced into the freshly prepared apparatus, melted and re-sublimed. The sublimed crystals were kept over phosphorus pentoxide until ready for use.

2. Kahlbaum's "Berylliumhydrat," containing a small amount of iron and some aluminum hydroxide, was treated direct with acetylacetonate. The reddish colour of the iron salt became immediately apparent, and the main part of the beryllium hydroxide was converted into the acetylacetonate. Some aluminum hydroxide was also converted into aluminum acetylacetonate, although Urbain and Debiere state that the aluminum derivative is not easily prepared from the hydroxide (*Comptes Rendus*, cxix., 302—305). The acetylacetonate was dissolved in alcohol, filtered, and crystallised, rejecting the mother-liquor which contained almost all of the small amount of iron and aluminum acetylacetonates. The deep red colour of the iron salt is a very delicate test for the presence of iron, even the slightest traces in an otherwise apparently pure beryllium carbonate being made evident at once by the yellowish tinge of the acetylacetonate. The crystals, still slightly coloured, were pulverised and washed in water in which the iron salt is much more soluble, and again crystallised from alcohol. This was repeated until crystals were obtained which yielded a clear colourless solution in absolute alcohol. These crystals were re-crystallised three times, as in preparation 1, were dried, sublimed, and re-sublimed, as already described. No evidence of any impurity could be found.

The Analysis.—The analyses were carried out in platinum crucibles without any transfer of material. The crucibles had been ignited for several hours in an atmosphere of hydrochloric acid gas containing a small amount of chlorine, to remove iron, after which they were submerged in fused acid potassium sulphate, cleaned, and finally boiled in concentrated hydrochloric acid. Light glass weighing bottles were procured of a convenient size to contain these crucibles, and in each was placed a thin porcelain dish, so that the crucibles could be enclosed in the weighing-bottles while still warm without danger of fracturing the glass. A platinum cone was weighed with each crucible. Before each weighing, the weighing-bottles and contents were placed in a desiccator over phosphorus pentoxide, the desiccator being so constructed that the bottles could be closed before removal, and the air of the desiccator, which always contains some moisture after being opened, replaced by perfectly dry air before the crucibles had cooled. The crucibles were placed in the desiccator warm before each weighing, except the initial weighing of the acetylacetonate.

Beryllium acetylacetonate is not hygroscopic, nor is the oxide, although Nilson and Petersen seem to have had a contrary experience (*Ber.*, xiii., 1451). Still every precaution was taken to have the conditions of weighing as nearly identical as possible. As before stated, all weighings were made by the method of substitution and

* From the *Journal of the American Chemical Society*, xxvi., No. 7.

against a tare treated in like manner and of the same material and shape, and of but slightly greater mass than the weighing-bottles and contents against which it was balanced. The crucible forming a part of the tare was not blasted.

After standing for some hours in the desiccator, the weighing-bottles, containing the empty crucibles and cones, were closed, removed, placed in the balance case, and after standing for one-half hour were weighed. The acetylacetonate was now placed in the crucibles, and the whole returned to the desiccator and allowed to stand for at least twelve hours, when they were again closed, removed, and weighed. Although subsequent weighings were always made, there was no further loss in weight.

The crucibles were then taken from the weighing-bottles, and re-distilled pure nitric acid, leaving no residue on evaporation, was added. The acetylacetonate dissolved to a perfectly colourless solution, which was diluted with twice its own volume of water, that had been re-distilled through block-tin and caught in platinum. The crucibles and contents were then placed upon a small platinum dish in an air-bath at 50°. It was kept at this temperature for from twenty-four to forty-eight hours, a further addition of water being once made. During this heating the acetylacetonate was almost completely evaporated. Any considerable rise in temperature caused the nitric acid to attack the liberated acetylacetone, decomposing it with foaming, which invariably ruined the determination. If the temperature was carefully regulated, however, no trouble whatever was experienced. After the removal of the acetylacetone, the temperature was slowly raised during another forty-eight hours to 100°, which served to remove most of the remaining liquid, leaving a clear glucose-like nitrate already basic in character from loss of nitric anhydride.

Perforated platinum cones, previously weighed with the crucibles, and of such size and shape that when inserted they fitted tightly in the crucibles above the nitrate, were now placed in an inverted position in the crucibles and the temperature again gradually raised during several hours to 175°. The use of the cones was thought advisable from noticing in a preliminary experiment that the last traces of water escaped through the viscous material in small bubbles, and it was thought that possibly in breaking, a loss might occur through spurting. The inner surface of the cones showed no trace of this, however, when later removed. The heating to 175° left the nitrate as a slightly porous white solid which had already lost more than 75 per cent of the nitric anhydride, equivalent to the beryllium present. The crucible was next supported in a Jannasch beaker upon a platinum triangle, and slowly heated over a Bunsen burner to decompose the last traces of nitrate, which was accomplished at a low heat and without any danger of loss of material. The crucible and contents were finally placed inside of a second platinum crucible, as recommended by Brauner (*Ann. Chem. Soc.*, lxxxi., 1249), to prevent loss of weight of the crucible itself, as Beilstein (*Chem. Centrbl.*, 1880, p. 614) and Hall (*Journ. Am. Chem. Soc.*, xxii., 496) have shown can so easily occur, and the whole blasted at a bright red heat until the crucible and contents showed no further loss of weight.

Corrections.—All weights are corrected to a vacuum standard, and the weights of beryllium oxide are also corrected for occluded gases.

Specific Gravity.—Unexpected difficulty was encountered in determining the specific gravity of the beryllium acetylacetonate, as no liquid could be found in which it was insoluble. It was but very slightly soluble in water at 20°, and it was found necessary to determine its specific gravity in an aqueous solution of itself at this temperature. This was not all that could be desired, but gave results which vary but little from the truth, and introduce an error into the subsequent corrections of weight so small that it can be entirely disregarded. In determining the specific gravity of the water, saturated with beryllium acetylacetonate, the pycnometer was filled to a mark on its outer surface and

evacuated for the same length of time as employed in the actual determinations of the specific gravity of the solid. No acetylacetonate separated. The pycnometer was then filled as usual, and its weight determined. The average of closely agreeing determinations gave sp. gr. $\text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2 = 1.168$ compared to water at 4°. The determination of the specific gravity of beryllium oxide needs no special comment. Krüss and Morath obtained the value 2.9644 (*Liebig's Ann. Chem.*, cclxii., 57). My results gave sp. gr. $\text{BeO} = 2.9640$, compared to water at 4°.

Occluded Gases.—Richards has shown that oxides, derived from the ignition of nitrates, contain occluded nitrogen and generally oxygen (*Am. Chem. Journ.*, xx., 702). Beryllium oxide is no exception to this rule, but the conditions of its formation by the very slow and gradual decomposition of the nitrate were peculiarly favourable to the removal of these gases. Gas was evolved on solution in strong sulphuric acid to the extent of 0.35 c.c. for each grm. of beryllium oxide, of which almost exactly one-third was soluble in alkaline pyrogallate. A correction was therefore made on the weights obtained of 0.00047 grm. per grm. of BeO .

No.	$\text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2$ Grms.	BeO Grm.	BeO Per cent.	Equivalent. BeO .
1. . . .	2.62245	0.31798	12.125	25.122
2. . . .	3.28037	0.39757	12.119	25.129
3. . . .	2.08993	0.25286	12.099	25.081
4. . . .	2.41401	0.29233	12.109	25.105
5. . . .	1.61353	0.19554	12.118	25.127
6. . . .	1.39714	0.16905	12.100	25.083
7. . . .	1.85023	0.22419	12.117	25.122

Mean 25.113

Analyses 1, 2, 3, 4, and 5 were made on Preparation 1.

Analyses 6 and 7 were made on Preparation 2.

The Properties and Analysis of Beryllium Basic Acetate.

Properties.—This unique and interesting chemical compound appears to be peculiar to beryllium alone. It was discovered by Urbain and Lacombe in 1901 (*Comptes Rendus*, cxxxiii., 874), and Lacombe a year later, (*Ibid.*, cxxxiv., 772), produced the basic formate, propionate, butyrate, isobutyrate, and isovalerianate of the same type. The formate having the highest percentage of beryllium would be excellent for determining the relative proportion of that element, but unfortunately it sublimates at so high a temperature, and consequently condenses so quickly, that it is extremely difficult to purify, especially as it is quite easily decomposed, even under much reduced pressure, at the temperature required for its sublimation. The basic acetate, however, has properties peculiarly fitting it for very complete purification, and also contains nearly twice as great a percentage of beryllium as any substance heretofore used for the determination of the atomic weight.

Basic beryllium acetate, $\text{Be}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$, melts at 283—284°, and boils at 330—331° (*Comptes Rendus*, cxxxiii., 874), and is readily sublimed without decomposition. It is itself almost insoluble in water, but is slowly hydrolysed by cold water, and quickly by hot, after which it dissolves. It is easily soluble, unchanged in absolute alcohol and in chloroform, and is soluble in all the solvents already mentioned for the acetylacetonate (see ante). It is also soluble in acetic anhydride and glacial acetic acid. Although a basic compound, its solution in glacial acetic acid can be saturated with hydrochloric acid gas and remain unchanged. It has not been found possible to produce the normal salt. It is unaffected in dry air. Ordinary acids attack it, setting free acetic acid, probably through the agency of water they contain. It is much more soluble in boiling glacial acetic acid than in cold, and is most readily crystallised in this manner. On cooling, it separates from boiling glacial acetic acid as small shining grains which, under a magnifying glass, are seen to be almost perfect octahedrons.

Preparation of Material.—1. Basic beryllium carbonate

prepared, as already described, from "Kahlbaum's hydrate" was dissolved in pure concentrated hydrochloric acid, ether added, and the small amount of aluminum, which it still contained, was separated by Havens' method (*Zeit. Anorg. Chem.*, xvi., 15-18; *Am. Journ. Sci.*, 4, v., 111-114). The pure chloride was precipitated by ammonia, dissolved in ammonium carbonate, ammonium sulphide added, allowed to stand, filtered, and boiled to precipitate the carbonate. The carbonate so produced was thoroughly washed with carefully purified water, and dissolved in excess of Kahlbaum's "Eisessig," which had been re-distilled and which left no residue on evaporation. The excess of glacial acetic acid was boiled off, with constant stirring, by means of a Bunsen burner held in the hand under the porcelain evaporator, and the residue dried. A large excess of glacial acetic acid was now added and boiled. Solution immediately took place, and, on cooling, the basic salt crystallised out in small shining octahedrons, which in the mass much resembled granulated sugar. The mother-liquor was rejected and the crystals washed with cold glacial acetic acid. They were again twice dissolved in hot, and re-crystallised in cold glacial acetic acid, rejecting the mother-liquors, and washing as before. The basic acetate so produced was dried at 150° to remove all excess of acid. It was then twice sublimed in Jena glass under a pressure of 250 m.m., and in a current of dry air free from water and carbon dioxide. The sublimation was brought about by means of a bath of cylinder oil maintained at a temperature varying little from 290°. The perfectly white crystalline product so obtained was kept over phosphorus pentoxide until wanted.

2. Another lot of the acetate was prepared in a manner differing little from that already described, except that it was sublimed at normal pressure, and the bath kept at 305-310°.

Analysis of the Basic Acetate.—The method used for the analysis of the basic acetate was almost identical with that employed for the acetylacetate. The initial temperature was 70°, however, as the decomposing action of the nitric acid was no longer to be feared. At this temperature most of the acetic acid was removed, but to be sure that no acetate remained undecomposed, concentrated nitric acid was added twice more, and the evaporation repeated. The basic acetate dissolved readily in nitric acid to a colourless nitrate.

Corrections.—The specific gravity of the basic beryllium acetate was determined in gasoline in which liquid it is less soluble than in any other investigated. Unfortunately, it is slightly soluble in this liquid, 50 c.c. dissolving 0.054 grm., and the gasoline was first saturated with the basic acetate before its own gravity was determined. Closely agreeing results yielded specific gravity $\text{Be}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ 1.362. Determinations of the gases, occluded by the oxide produced from the basic acetate, agreed with those from the acetylacetate. In fact, the figure given is the average of several results on both. The variation of all results was from 0.32 to 0.39 c.c. per grm. of oxide. Occluded gases = 0.0047 grm. per grm. BeO .

Analyses of Basic Beryllium Acetate.

No.	$\text{Be}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ Grms.	BeO Grm.	BeO Per cent.	Equivalent. BeO .
1. . . .	1.89291	0.46788	24.717	25.139
2. . . .	1.47931	0.39534	24.703	25.111
3. . . .	1.09012	0.26911	24.686	25.097
4. . . .	1.35642	0.33493	24.692	25.105
5. . . .	1.56787	0.38715	24.693	25.106
6. . . .	1.34465	0.33204	24.693	25.106
7. . . .	2.61484	0.64630	24.716	25.137
8. . . .	2.67721	0.66109	24.693	25.107
9. . . .	3.11534	0.76930	24.693	25.107
Mean				25.113

Results 1 to 6 were obtained on Preparation 1.
Results 7 to 9 were obtained on Preparation 2.

Atomic Weight of Beryllium.

(O = 16, H = 1.008, C = 12.01).

From acetylacetate.	From basic acetate.
9.142	9.139
9.120	9.111
9.081	9.097
9.105	9.105
9.127	9.106
9.083	9.106
9.122	9.137
Mean 9.113 ± 0.0059	9.107
	9.107
	Mean 9.113 ± 0.0033
	General mean $\text{Be} = 9.113 \pm 0.0043$

Samples of the oxide produced from both the beryllium acetylacetate and the basic acetate were dissolved in pure hydrochloric acid, and sent to Prof. Charles C. Hutchins, of Bowdoin College, who kindly consented to examine them with the special spectroscopic facilities at his command. He reported that they were absolutely free from iron and aluminum, and that he was unable to find any other impurity. My acknowledgment and sincere thanks are due to him for this part of the work.

In connection with this investigation I have prepared a bibliography of beryllium, with abstracts, which I believe to be complete, and which will shortly be published separately.

THE OCCURRENCE OF PLATINUM IN
WOLLASTONITE ON THE ISLAND OF SUMATRA,
NETHERLANDS EAST INDIES.*

By L. HUNDESHAGEN.

WHEN visiting Western Sumatra in 1901, the author's attention was drawn to the unusual conditions under which a deposit of wollastonite and grossularite occurs, and, on the opportunity arising, a further study of the ground was made last year (1903). The deposit is situated near the high road, at the Singenggo river, west of the village Moeara Sipongi (Japanoei), and about 35 English miles from the sea coast, and in former times was mined by the Malays. It contains gold, also small quantities of platinum.

The main features of the ore deposit, which is composed chiefly of grossularite, are the following:—

At 30 m. to the south-west occur old schists, having a strike of north 70° W. These are older than the granites which in many parts of the district are met with at the same or at a much higher elevation. To the north the ore deposit has been sharply and almost vertically cut off by a well-defined dyke of hornblende rock, which is in some places slightly silicified, but contains no garnet, and shows no transition into the ore body. On the west the ore deposit is covered by a cap of a blackish angite-diorite, under which in one place a little granite outcrops, while almost the whole is buried under the products of an enormous extinct volcano. Its crater-lake on the Malintang mountain is 1.2 km. long and 0.7 km. wide, and lies 19 km. due south. Far to the north of the ore deposit, primitive and Cambrian schists are met with, and also some remnants of the carboniferous limestone series.

Upon a consideration of the facts, the author is of opinion that the present ore deposit was originally a layer, or a big lens, of limestone imbedded in the old schists, which has, by apophyses of granite, been altered into garnet and wollastonite, being at the same time, or very soon afterwards, mineralised by hot solutions carrying copper, gold, platinum, &c. This Singenggo ore deposit, therefore, differs in some respects from other garnet,

* A Paper read before the Institution of Mining and Metallurgy, July 21, 1904.

wollastonite deposits (mostly from 9 to 15 km. distant) which all belong to the carboniferous limestone series, and may, though very old, be considerably younger than the Singingoe deposit.

The almost horizontal but undulated zone of contact between the grano-diorites and limestones has been fairly well disclosed by both ancient and recent workings, which have also exposed some long apophyses of diorite and wollastonite. All the characteristics of a very intense, although local, metamorphism are noticeable at the base of both the carboniferous limestone and the clay slates. The more recent auriferous garnet and wollastonite contact deposits referred to never seem to carry the platinum metals, although they frequently contain copper, and sometimes traces of nickel and cobalt.

The Singingoe ore, which assayed platinum, is composed of the following minerals:—

85 per cent to 88 per cent wollastonite, interlaced sometimes with bornite; 12 per cent to 14 per cent grossularite.

Traces to 5 per cent bornite, with secondary incrustations of copper glaucite.

Traces of magnetite, iron pyrites, manganese (braunite and rhodonite),* and calcite. Arsenic being absent, nothing points to the presence of sperrylite. Occasionally vugs and veins of calcite occur, with large crystals of pyroxene.

The analysis of a practically pure sample of colourless tough wollastonite gave:—

	Per cent.
Loss after heating	0.02
SiO ₂	51.48
CaO	47.61
Oxide of manganese	0.60
Magnesia	Minute trace*
Oxide of iron and alumina	0.24

The absence of magnesia in a platinum ore is rather striking, the more so as white and yellow pure serpentine rocks are met with in the vicinity in primitive schists, and, further, because a well-crystallised white magnesite occurs only a few hundred metres from the Singingoe wollastonite deposit. Besides, carbonate of magnesia sometimes occurs here in contact deposits containing copper and iron pyrites, asurite, magnetite, &c.

It may further be worth mentioning that a sample of slightly decomposed wollastonite with no copper, or only minute traces of that metal, proved to be richest in platinum, the assay showing:—

6 grms. Pt per 1000 kilos.
4 " Au "
2 " Ag "

while, on the other hand, selected samples with 2 to 10 per cent of bornite and malachite contained—

15 to 2300 grms. Au per metric ton,
15 to 560 grms. Ag "

and only traces of platinum.

Auriferous garnet, poor in wollastonite, appears to contain no platinum.

In this section no platinum could be detected under the microscope; nor could any be seen when finely powdered ore was concentrated in the wooden batea.

About 10 to 25 m. from the outcrop, the concentrated river sand shows small particles of whitish crystalline gold and rounded grains of white platinum, the latter varying from 0.1 to 0.3 m.m. in size.

In Western and South-Eastern Borneo, where platinum is met with in diamond placers, it is not found in the form

of grains, but in thin scales, ranging from 0.1 to 1.0 m.m. in thickness.

These platinum scales contain amongst other usual metals, copper varying from 3.8 to 4.5 per cent, evidently as an alloy, since the copper cannot be extracted by strong nitric acid.

Although peridotites (serpentine) abound in Borneo, no platinum could be found by the author in their close vicinity, but only traces of gold and metallic copper. The diurnal platiniferous placers are found at a considerable distance, say 10 to 30 km., from the deposit described.

All this points to the probability that in the Indian Archipelago the occurrence of platinum is unusual, and that where found the metal is not derived from serpentines.

METHOD FOR THE ESTIMATION OF PRUSSIAN BLUE.

By CH. COFFIGNER.

FOLLOWING my paper on the solubility of Prussian blue (*Bull. Soc. Chim.*, vol. xxvii., p. 696) appeared a note by M. Wyruboff (*Ibid.*, p. 940), in which, before asking certain questions to which I am about to give an answer, he remarked that he had already announced the solubility of Prussian blue in hydrochloric acid.

At the time I published my paper I was unaware of M. Wyruboff's work, and I had read in the principal textbooks on chemistry, as well as in special works on the colour industry, that Prussian blue was insoluble in hydrochloric acid.

M. Wyruboff states that it would be interesting to submit solutions of blue in mixtures of HCl + fatty alcohols to the action of cold. I had already thought of that, and had asked M. Claude to be good enough to submit solutions containing 20 grms. per litre to the lowest possible temperatures. In every case the result obtained was invariable: solidification of the solution without any change of colour.

When we add a small quantity of water to alcoholic solutions, the Prussian blue is precipitated. M. Wyruboff asks whether the solution contains ferric chloride.

I have entirely re-examined this question of precipitation by water, using blues from Berlin sold as pure by different makers.

I dissolved 0.5 grm. of blue in 50 c.c. of solvent, precipitated with water, washed until all acid reaction disappeared, and collected the precipitate on a tared filter.

The following results were obtained with the same blue:—

Alcohols used.	Weight of blue obtained.
Isobutylic	0.487 grm.
Amylic	0.498 "
Propylic	0.480 "

The filtration is very difficult. After the second washing the blue will not settle, and it is impossible—even after passing it through the filter several times—to obtain a perfectly colourless filtrate. I have tried using double filters, or the addition of a known quantity of sulphate of baryta, without obtaining any better results.

I succeeded in the filtration, without any loss, by using alcohol for the second and subsequent washings. This simple plan succeeds perfectly, and if, in very rare cases, the first liquor passes a little blue, it is sufficient to wait until the next day; the blue, in small amount, becomes united on the surface or at the bottom, and is easily collected on the filter.

I have operated on several blues of different manufacture in this manner, always using the same dissolving mixture—hydrochloric acid and propylic alcohol, this alcohol having the advantage over amylic alcohol of its greater solubility in water. The following are the results obtained:—

* In some samples of the garnet rock more recently analysed, after separation from the accompanying minerals, the garnet has been found to contain 0.19 per cent of magnesia (MgO), which small proportion is, according to the author's theory, to be accounted for by the biotite of the intrusive granite.

Mark.	Weight of blue dissolved.	Weight of blue recovered.	Blue, per cent.
B.	0.5	0.490	98.0
B.	0.5	0.491	98.2
P.	0.5	0.502	100.4
P.	0.5	0.502	100.4
S.	0.5	0.501	100.2
S.	0.5	0.502	100.4
M.	0.5	0.498	99.6
M.	0.5	0.501	100.2

These results make it clear that it is possible to use dissolving mixtures as a method of estimation.

The principal blue colours containing Prussian blue are the following:—

Charron blue ..	Prussian blue and sulphate of baryta.
Mineral blue ..	Prussian blue, kaolin, and sulphate of baryta.
Paris blue ..	Prussian blue and alumina.
Blue fecula ..	Prussian blue and starch.

These compositions are not absolute and may vary with different makers; but, on the whole, besides pure blue, we find sulphate of baryta, carbonate of lime, sulphate of lime, kaolin, alumina, and starch.

I have prepared the following series of mixtures with one or more of the above-mentioned substances:—

1.	Prussian blue	1.400 gm.
	Sulphate of lime	0.600 "
2.	Prussian blue	1.200 "
	Kaolin	0.800 "
3.	Prussian blue	1.000 "
	Starch	1.000 "
4.	Prussian blue	0.550 "
	Sulphate of lime	0.200 "
	Carbonate of lime	0.200 "
	Kaolin	0.600 "
	Alumina	0.450 "
5.	Prussian blue	0.300 "
	Carbonate of lime	1.700 "
6.	Prussian blue	0.250 "
	Sulphate of baryta	1.750 "
7.	Prussian blue	0.150 "
	Kaolin	0.400 "
	Sulphate of baryta	1.000 "
	Alumina	0.400 "
	Carbonate of lime	0.050 "
8.	Prussian blue	0.060 "
	Sulphate of baryta	1.940 "

I attacked 2 grms. of each of the above mixtures with 100 c.c. of the solvent. When the whole of the blue had gone into solution I made the bulk up to 200 c.c. If the charge goes into solution with the blue, as in the case of the carbonate of lime and the starch, I take 100 c.c. and precipitate with water; the blue only is precipitated. If the charge is not attacked, I filter, collect 100 c.c. in a graduated flask, and precipitate with water. After washing with water and alcohol until the acid reaction has disappeared, the blue is collected on a tared filter and weighed after drying in the oven at 100°. The following results were obtained with the mixtures of which the composition is given above:—

No.	Amount of blue used.	Amount of blue found.
	Per cent.	Per cent.
1	70.0	69.80
2	60.0	60.30
3	50.0	50.20
4	27.5	27.45
5	15.0	14.80
6	12.5	12.30
7	7.5	7.45
8	3.0	2.70

I used this method for the analysis of a commercial "Charron blue," and I found—

Moisture	0.22
Insoluble portion	94.82
Prussian blue	4.30
	99.34

Not at all a bad result when we consider that the natural sulphate of baryta which forms the insoluble portion always contains a little sulphate of lime and oxide of iron.

Remarks.

When we have to deal with a blue containing alumina, the solution takes place much more slowly. For example, if we take 1.600 grms. of Prussian blue and 0.400 gm. of alumina, it is impossible to get all the blue into solution with 100 c.c. of the solvent, even when prolonging the boiling for a considerable time. On the other hand, the solution is soon effected by replacing the alumina by the same proportion of sulphate of baryta, kaolin, &c.

The quantity of water to be added to effect the precipitation varies according to the richness of the solution. I have been surprised at the large amount of water necessary to precipitate solutions slightly concentrated. For this reason I have determined, as accurately as possible, the amount of water necessary to precipitate 50 c.c. of solutions of different strengths. The following table gives the figures obtained:—

Strength of the solution	Water necessary.	Strength of the solution.	Water necessary
Per cent.	C.c.	Per cent.	C.c.
0.1	79.0	0.7	14.5
0.2	46.5	0.8	12.5
0.3	26.5	0.9	11.0
0.4	23.5	1.0	8.0
0.5	20.5	1.5	5.5
0.6	17.0	2.0	2.5

As we add the water the solution becomes deeper and deeper in colour, passing to reddish brown, and finally to deep green immediately before the precipitation of the blue. These changes of colour, especially with solutions of slight concentration, make it very difficult to seize the exact moment of precipitation. The rapidity with which the water is introduced is also a factor to be considered. Finally, it may also be remarked that a smaller quantity of water allows the precipitation to go more slowly.

If we construct a curve, making the abscissae the strengths of the solutions, and the ordinates the number of cubic centimetres of water necessary for their precipitation, we observe a very rapid fall for solutions of 0.1, 0.2, and 0.3 per cent. After this, the variations become very regular.

The liquor separated from the blue precipitate is colourless or of a very slight greenish tint. On concentration it changes to yellow. When all the alcohol has been driven off by boiling, the liquid, almost completely neutralised with carbonate of soda, contains ferric chloride, which is easily detected by means of ferrocyanide and sulphocyanide.

The figures given above prove the complete precipitation of the blue, so that we can only attribute the presence of iron in the aqueous portion to two causes:—(1) To the presence of small quantities of ferrous chloride, which is to be found in nearly every sample of Prussian blue; (2) to a decomposition of a small portion of the blue by hydrochloric acid.

I have been able to prove these suppositions by experiment. For the first, it suffices to exhaust the Prussian blue with water; the aqueous portion gives a slight white precipitate with ferrocyanide—if not with all commercial blues, at any rate with a large number of them. To prove the second case I dissolved a few milligrams of blue in a large excess of hydrochloric acid. The solution is not precipitated by water. When concentrated and neutralised, ferrocyanide and sulphocyanide both give the characteristic reactions of the ferric salts.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 7.

THE MECHANICAL ANALYSIS OF SOILS.

By JOHN GEDDES MCINTOSH.

Too much stress should not be given to the mechanical analysis of soils. Man is not an automatic machine, and I am afraid few chemists would get identical results with the same soil in succession. That they do not get it by adopting different methods each of which is a standard method in its way is evident from the following results with the same soil from the neighbourhood of Pisa, quoted by Peligot:—

	I. Per cent.	II. Per cent.	III. Per cent.
Sand	1'47	32'07	13'35
Clay	87'31	37'67	71'90
Earthy carbonates	—	20'20	—
Organic and volatile matter	9'66	10'25	—
Undetermined	—	—	14'75
Soluble matter and loss	1'56	—	—
	100'00	100'19	100'00

I. Nobel's process. II. Schloesing's process. III. Masure's process.

Working with an upward current of water I have found comparative results cannot be obtained unless the pressure of the current of water remain constant, a desideratum difficult to realise. Moreover, the data afforded by a mere mechanical analysis of the soil tells nothing either to the chemist or farmer. No one is able to picture in his mind's eye the appearance and properties of a soil from its mechanical analysis. An expert agriculturist by a single glance at a soil can form an opinion regarding it far more superior and valuable than any which he, aided by the most expert agricultural chemist extant, can possibly form from inspecting the results of a mere mechanical analysis alone. Land valuers do not make mechanical analysis of soils.

Analytical Laboratory,
9, Parsonage Street, Cubitt Town, E.

ANALYSIS OF KUNZITE.

By R. O. E. DAVIS.

At the request of Professor Charles Baskerville, Director of the Chemical Laboratory, I undertook the chemical analysis of kunzite, the new and beautiful variety of spodumene, described by Kunz and himself (see *Am. Journ. Sci.*, vol. xviii., July, 1904; also *Science*, 1903, xviii., 303 and 769). The methods used were those given in Hillebrand's excellent "Principles of Rock Analysis" (*Bull. U. S. Geol. Survey*, No. 176), and need not be re-stated here.

A selected, clean, deep lilac-coloured crystal, quite free from flaws, was ground to an impalpable powder and used in the analytical work. Following are the figures obtained:—

	Per cent.
SiO ₂	64'05
Al ₂ O ₃	27'30
NiO	0'06
MnO	0'11
ZnO	0'44
CaO	0'80
MgO	none
K ₂ O	0'06
Na ₂ O	0'30
Li ₂ O	6'88
Loss on ignition	0'15
Total	100'15

No chromium, vanadium, titanium, iron, strontium, barium, thorium, zirconium, or phosphorus was found. On account of the unique properties possessed by the mineral the other rare earths were looked for. Dr. W. J. Humphreys, of the Rouss Physical Laboratory of the University of Virginia, kindly photographed the arc spectrum obtained from the material which had been freed from silicon and lithium. He reported none of the characteristic lines of cerium and yttrium groups present. The material lost its pink colour on ignition.—*American Journal of Science*, vol. xviii., July, 1904.

THE BRITISH SCIENCE GUILD.

It has been a frequent subject of comment that, although the contribution of this country to the progress of science has been second to that of no other nation, the English people do not manifest that interest in, and belief in the powers of science, which are noticeable among the peoples of the Continent, or of America. In spite of the efforts of many years, the scientific spirit, essential to all true progress, is still too rare, and, indeed, is often sadly lacking in some of those who are responsible for the proper conduct of many of the nation's activities. It is with the view of attempting to remedy this evil, and to bring home to all classes the necessity of applying scientific treatment to affairs of all kinds, that the proposal is made to bring together those convinced of this necessity by founding "The British Science Guild."

The objects and organisation of the Guild, which will be entirely disconnected from party politics, are as follows:—

Objects.

1. To bring together as members of the Guild all those throughout the Empire interested in science and scientific method, in order, by joint action, to convince the people, by means of publications and meetings, of the necessity of applying the methods of science to all branches of human endeavour, and thus to further the progress and increase the welfare of the Empire.
2. To bring before the Government the scientific aspects of all matters affecting the national welfare.
3. To promote and extend the application of scientific principles to industrial and general purposes.
4. To promote scientific education by encouraging the support of universities and other institutions where the bounds of science are extended, or where new applications of science are devised.

Methods of Attaining these Objects.—(a) By publications; (b) by Meetings; (c) by Conferences and Lectures; (d) by Deputations.

Organisation.

Admission of Members.—All British subjects, both men and women, are eligible for membership of the Guild; it is expected, however, that its members will be recruited principally from the following:—

The House of Lords; the House of Commons; Colonial Legislatures; County, District, Borough, and Parish Councils; Municipalities; Educational Committees; Scientific and Literary Societies and Organisations; Commercial and Industrial Chambers and Organisations; the Learned Professions; Universities, Colleges, Educational Bodies, and Graduates of all British Universities; Representatives of Labour.

At a meeting of the promoters of the Guild, held, by permission of the Officers, at the Rooms of the Royal Society, on April 20th, 1904, it was decided that the steps preliminary to the formation of the Guild should be taken by an Organising Committee, of which the following were appointed members, with power to add to their number:—Lord Avebury, F.R.S.; Professor W. E. Ayrton, F.R.S.; Sir George Sydenham Clarke, K.C.M.G., F.R.S.;

Captain E. W. Creak, R.N., C.B., F.R.S.; Mr. Clive Cuthbertson; Dr. William Garnett; Mr. Sidney Lee; Sir Norman Lockyer, K.C.B., F.R.S.; Lady Lockyer; Mr. N. Maccoll; Professor Raphael Meldola, F.R.S.; Professor J. Perry, F.R.S.; Sir Gilbert Parker, M.P.; Sir William Ramsay, K.C.B., F.R.S.; Dr. W. N. Shaw, F.R.S.; Professor S. P. Thompson, F.R.S.; Dr. Augustus Waller, F.R.S.; Sir Henry Trueman Wood.

The Organising Committee has elected Sir Norman Lockyer, President; Lord Avebury, Honorary Treasurer; Lady Lockyer, Honorary Assistant Treasurer; and Mr. C. Cuthbertson, Honorary Secretary.

It was resolved that Life Members of the Guild shall pay, on admission, two guineas, which includes a registration fee of 2s. 6d. and that Annual Subscribers shall pay, on admission, 5s., and in each subsequent year 2s. 6d. It was also resolved that donations may be accepted.

The Committee are now engaged in communicating with those corporate bodies and individuals whose support and sympathy are desired.

A General Committee will be appointed, which will subsequently select from among its members an Executive Committee for the management of the affairs of the Guild. The Executive Committee will meet from time to time as their Chairman may direct, and will formulate such rules as experience may suggest, for the approval of the General Committee.

The General Committee will probably take power to appoint or approve local and special committees, which will act as branches of the Guild.

The following have already signified their general approval of the objects and proposed organisation of the Guild:—

The Right Honourable Lord Alverstone, G.C.M.G.; The Right Honourable Lord Avebury, F.R.S.; Professor Ayrton, F.R.S.; Sir John Wolfe-Barry, K.C.B., F.R.S.; Dr. W. Blandford, F.R.S.; Sir James Blyth, Bart.; Mr. Brabrook, C.B.; Sir George Birdwood, K.C.I.E.; Sir John Brunner, Bart.; Sir Lauder Brunton, F.R.S.; Major-General Sir Owen Tudor Burne, G.C.I.E.; Sir Edward Busk; Mr. R. H. Caird; Sir William Church, Bart., K.C.B.; Sir George Sydenham Clarke, K.C.M.G., F.R.S.; The Hon. Sir John Cockburn, K.C.M.G.; Captain Creak, R.N., C.B., F.R.S.; Mr. Clive Cuthbertson; Professor W. E. Dalby; Dr. Ferrier, F.R.S.; Sir Michael Foster, M.P., F.R.S.; Dr. William Garnett; Sir Archibald Geikie, F.R.S.; Sir Robert Giffen, K.C.B., F.R.S.; Mr. Hammond-Chambers, K.C.; Professor Herdman, F.R.S.; Professor J. Larmor, F.R.S.; Dr. Sidney Lee; Sir Norman Lockyer, K.C.B., F.R.S.; Lady Lockyer; Dr. Lockyer; Mr. Maccoll, Professor R. Meldola, F.R.S.; Sir A. Noble, Bart., K.C.B., F.R.S.; Sir Gilbert Parker, M.P.; Professor Perry, F.R.S.; Sir William Ramsay, K.C.B., F.R.S.; The Lord Ray, G.C.S.I.; Sir Wemyss Reid; Sir William Richmond, K.C.B., R.A.; Sir Henry Roscoe, F.R.S.; Mr. E. Robertson, M.P.; Sir A. Rucker, F.R.S.; Dr. W. N. Shaw, F.R.S.; Mr. Alex. Siemens; The Lord Strathcona and Mount Royal; Sir L. Alma Tadema, R.A.; Professor Silvanus P. Thompson, F.R.S.; Dr. A. D. Waller, F.R.S.; Field-Marshal Viscount Wolseley, G.C.B.; Sir Henry Trueman Wood.

ascertained all the following physical properties of specimens of tempered steels, which had previously been very carefully analysed, viz., the microstructure, density, elasticity, hardness, electrical resistance, and magnetic properties, and gives in this volume the results obtained with such general conclusions as can be drawn from them. In successive chapters the methods of determining these constants are described, and the results obtained experimentally discussed at length, and finally an attempt is made to classify these properties and to draw conclusions of practical interest, especially as regards methods of testing steels, a subject of great technological importance. Though the actual outcome of the experiments does not appear to be any generalisation of much value, a great deal of careful work, both experimental and literary, has evidently been done in preparing this thesis.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). V. Band, 7 and 8 Heft. Edited by FRANZ Hofmeister. Braunschweig: Friedrich Vieweg und Sohn. 1904.

This number of the *Beiträge* contains many papers of great interest to physiological chemists. Among them may be mentioned one by Dr. Kammann on the hay fever poison contained in rye pollen. The author undertook researches to determine the proportion of this poison to the other constituents of the pollen, and to examine its characteristic properties. He is satisfied that he has proved that the poison is a toxalbumen, stable towards acids and enzymes, and capable of being heated to 70° without being destroyed. A most interesting paper on a subject of great importance is that by Sigval Schmidt-Nielsen, on the behaviour of the enzymes towards concentrated electric light. The experiments described were performed with Finsen's apparatus, as described in the "Mitteilungen aus Finsens Medizinischem Lichtinstitut," the enzymes examined being chymosin, chymosinogen, and anti-chymosin. This attack on some of the problems of light biology, though it shows conclusively that these enzymes are very easily influenced by concentrated electric light, unfortunately has, so far, given only somewhat contradictory results as concerns the question of the increase of the quantity of enzyme by physical means; nevertheless, a mass of valuable material has been collected, and further research may explain some of the difficulties which have cropped up in the course of the investigation. The same author communicates a short notice on the effect of radium rays on chymosin, in which he shows that exposure to such rays causes a slight but perceptible diminution in the effect of the ferment, i.e., increases the time of coagulation of goat's milk. A series of experiments carried out in the botanical institute of the University of Tokio is described by Dr. K. Shibata, who has succeeded in proving the existence in the mycelium of *Aspergillus niger* of an enzyme or enzymes capable of splitting off ammonia from urea, biuret, and some acid amides. To this group of enzymes, which he is further investigating, he proposes to give the name "amidases."

A Compendium of Chemistry, including General, Inorganic, and Organic Chemistry. By Dr. CARL ARNOLD. Translated by JOHN A. MANDEL, Sc.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

It is not easy to see what class of readers can be supposed to regard the purchase of this book as a profitable investment. It cannot be recommended for use as a text-book by students, being too condensed and too full of individual details regarding an immense number of substances to the exclusion of the consideration of general principles, except perhaps as regards the section on general chemistry, which contains a good deal of useful matter well put together, and though quite unobjectionable in most respects it presents no special novelty of treatment to recommend it.

NOTICES OF BOOKS

Recherches Physiques et Physico-chimiques sur l'Acier au Carbone. ("Physical and Physico-chemical Researches on Carbonised Steel"). By CARL BENEDICKS. Uppsala: Librairie de l'Université. 1904.

IN order to explain the relations of the physical properties of iron and steel to their chemical constitution, the author of this thesis rightly considers the logical method to adopt is to determine as many different properties as possible of the same specimen. Going upon this principle he has

While being too detailed for a students' text-book, as a work of reference it can hardly be regarded as sufficiently comprehensive, and chemists would probably prefer to possess a more specialised volume devoted exclusively to one branch of chemistry, though the fact that the original has run through eleven editions certainly shows that in some circles its merits, or rather its lack of demerits, are appreciated.

Chémie der Eiweisskörper. ("The Chemistry of the Albuminous Substances"). By Dr. OTTO COHNHEIM. Second Edition. Braunschweig: Friedrich Vieweg und Sohn. 1904.

ALTHOUGH only a few years have elapsed since the publication of the first edition of this work, our knowledge of the chemistry of the albumens has developed so rapidly as to render advisable the preparation of a second edition, for which it has been necessary to re-write many chapters, especially in that part of the book which describes the physical properties, constitution, and decomposition products of the albuminous substances in general. In the special part also a good many alterations have been made, which all tend to add to the value of the work, which is well qualified to hold a unique place in the literature devoted to this branch of chemistry. Current periodicals have been thoroughly well searched, some of the references even being to papers which appeared only in the early part of this year.

Die Galvanoplastik. ("Galvanoplastic"). By Dr. W. PFANHAUSER. Halle-a-S.: Wilhelm Knapp. 1904.

THE author of this monograph shows himself to be thoroughly conversant with the ins and outs of his subject, and is evidently competent to write authoritatively on it. Though the task of preparing this volume might easily have degenerated into a mere abstracting of patent literature, Dr. Pfanhauser has contrived to infuse quite another spirit into his work, and, while giving all necessary details regarding apparatus and methods, he has very wisely omitted to make mention of every modification of only slight importance; as, for example, in dealing with the constituents and their proportions in galvanoplastic baths, for which such numerous recipes differing to only a trifling extent are given by various authors. The methods of industrial importance are everywhere emphasised, and the short chapters on the applications of the process to the preparation of gramophone records, artificial teeth, &c., are written in a thoroughly practical spirit, which indeed is a marked characteristic of the whole book.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

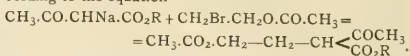
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 2, July 11, 1904.

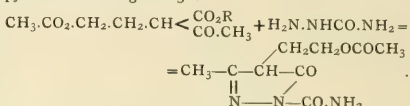
Thermo-chemical Investigations on Solution and Polymerisation of Cyanogen.—M. Berthelot.—The author measures the loss of energy when—(1) Cyanogen reacts on water, (2) potassium cyanide reacts on dissolved cyanogen, (3) cyanogen reacts on alcohol, and (4) potassium cyanide reacts on an alcoholic solution of cyanogen.

Condensation of Glycol Bromacetate with Acetoacetic and Acetonedicarbonic Ethers.—A. Haller and F. March.—When glycol bromacetate reacts on the sodium derivatives of methylenic compounds, products are obtained in which the quantity $-\text{CH}_2-\text{CH}_2\text{O}.\text{CO}.\text{CH}_3$ remains unchanged. In the case of sodium acetoacetic ethers

γ -acetoxybutyrate of the acetyl- α -acetyl are obtained according to the equation—



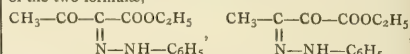
Compounds which, with semicarbazide, give a single pyrazolone melting at 163° :—



Densities of Sulphurous Anhydride and Oxygen.—Adrien Jaquero and Alexandre Pintza.—The authors re-determine the density of sulphurous anhydride and oxygen. In the case of oxygen the mean of five experiments gives the value 1.4292 grms. as the weight of a litre of this gas at 0° and under a normal pressure (latitude 45° and at sea level). The concordance of the individual results is not so good as in the case of sulphurous anhydride—the maximum exceeding the mean by $1/3000$ part. This fact possibly proves the existence of traces of solid particles in the gas, which causes the mean value to be slightly higher than numbers obtained by other experimenters—Lord Rayleigh, 1.42907 ; Leduc, 1.4288 ; Morley, 1.42900 . The number obtained for sulphurous anhydride under the same conditions is 2.92664 .

Heat of Combustion of Sulpho-organic Compounds.—P. Lemoult.—The author measures the heat of combustion of amyl mercaptan, amyl sulphide, methyl sulphocyanate, and other organic sulpho-compounds by applying the following formula:—For compound $\text{C}_x\text{H}_y-\text{a}(\text{N}_m\text{H}_a)_n$, the heat of combustion is given by $z = 102x + \frac{55}{2}y + (16.5m - 10a) + 151n$.

Reactions of $\alpha\beta$ -Diketo-butyric Ethers. I. Action of Phenylhydrazine.—L. Bouveault and A. Wahl.—In a preceding research the authors showed that the action of nitrous anhydride on acetylacetic ethers under certain conditions leads to the formation of $\alpha\beta$ -diketo-butyric ethers, $\text{CH}_3-\text{CO}-\text{CO}-\text{COOR}$. They also found that these ethers react with phenylhydrazine in the cold, giving mono-phenylhydrazones, of which the constitution has not been established. Diketonic ethers contain two carbonyl groups capable of reacting with phenylhydrazine, and it is apparent that the constitution of the hydrazones corresponds to one of the two formulæ,—



according as the reaction takes place on the α - or β -carbonyl group. The authors' experiments prove this to be the case.

Researches in the Pyrane Series.—E. E. Blaise and H. Gault.—The authors obtain certain simple derivatives in the pyrane series, beginning with the first term of the

series, pyrane, $\text{O} < \begin{array}{c} \text{CH}=\text{CH} \\ \text{CH}=\text{CH} \end{array} > \text{CH}_2$. Their experiments were

first attempted on dicarboxyl-1.7-diketonic-2.6-acids, from which the pyranic acids should be obtained, the condensation being effected with 1.5-diketones, and which should result in the cyclohexenones. These experiments were not satisfactory, and they therefore condensed the different aldehydes with oxalacetic ether.

Certain Phenolic Ethers with Pseudo-allylic Chain, $\text{R}-\text{C}(\text{CH}_3)=\text{CH}_2$.—MM. Béhal and Tiffeneau.—During the reaction of methyl-magnesium iodide on the corresponding ether salts, besides the tertiary alcohols, $\text{R}-\text{C}(\text{OH})(\text{CH}_3)_2$, a larger or smaller quantity of a pseudo-allylic derivative, $\text{R}-\text{C}(\text{CH}_3)=\text{CH}_2$, is obtained. In

order to obtain a maximum amount of this latter substance, the authors find it necessary to use one or two extra molecules of the methyl-magnesium iodide. They obtain the following bodies, and find their boiling-points, densities, and indices of refraction:—

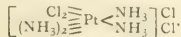
	Boiling-point.	Density.	Refractive index.
Ortho-pseudo-allylanisol	198—199	0.983 at 21°	1.5315
Meta-pseudo-allylanisol.	215—216	1.009 at 0°	1.5417
Para-pseudo-allylanisol.	223	Melts at 32°	1.5423

Action of a Trace of certain Salts and Caustic Alkalis on Diphenylcarbonic Ether.—R. Fosse.—In a preceding research the author discovered that when diphenylcarbonic ether is heated in contact with a small quantity of dry sodium carbonate, a curious transformation into carbonic anhydride, phenol, and phenylorthophenoxycarbonate takes place quantitatively, according to the reaction $2\text{CO}_2(\text{C}_6\text{H}_5)_2 = \text{CO}_2 + \text{C}_6\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{O}-\text{C}_6\text{H}_5$. The author now extends his experiments, and investigates the effect of traces of other substances—trisodic phosphate, disodic arsenate, sodium bi- and tetra-borate—on diphenylcarbonic ether.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxvii., No. 10, 1904.

Fatty Aromatic Diazo-amido Compounds (Triazines).—Ludwig Wolff and Hans Lindenhayn.—If 50 grms. of diazo-benzene-imide to which 200 grms. of alcohol have been added, are heated to boiling with a solution of 30 grms. of potassium cyanide and 5 grms. of potassium hydroxide in 50 grms. of water for half-an-hour, and then about half the alcohol distilled off, on cooling glittering scales of the potassium salt of 1-phenyl-2-cyantriazine separate out. The triazine itself is obtained by the addition of hydrochloric or acetic acid to the ice-cold, very dilute solution of the potassium salt. It is very unstable, and gradually changes into a brown mass insoluble in soda. From the potassium salt the methyl ester was also prepared. The latter gives methylaniline, nitrogen, and cyanic acid on addition of acids or bases; on the other hand, the phenyl-cyantriazine itself gives, with mineral acids in the cold, diazobenzene and urea. Hence, the two substances probably differ in constitution, as shown by the formulæ $\text{C}_6\text{H}_5\text{N}:\text{N}:\text{NH}:\text{CN}$ and $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{N}:\text{N}:\text{CN}$. The authors are led to think that the potassium salt and the free acid are similarly constituted, though they cannot positively prove this.

Notes on Ammoniacal Platinum Compounds.—Hans and Astrid Euler.—On evaporation of the filtrate from Magnus's salt from the saturated ammonium chloride solution, a brick-red powder separates out, if platinum chloride, as well as platinumous chloride, is present (Grimm). If the aqueous solution of the red powder, even when saturated with ammonium chloride, is evaporated, the residue consists partly of yellowish-red scales and partly of a yellow crystalline powder. These crystals have the same empirical composition as Grimm's red powder, $\text{Pt}(\text{NH}_3)_4\text{Cl}_4$. The scales have the same percentage of platinum as the yellow powder, from which about half the chlorine may be precipitated with silver nitrate. If fairly concentrated sulphuric acid is added to the solution of the yellow salt fine red needles separate out, which become white and opaque in cold water and turn red again in hot concentrated sulphuric acid, and are therefore chloro-diplatinamine sulphate. Hence the yellow substance, which is formed by transposition from Grimm's red powder, is chloro-diplatinamine chloride.—



and not a double salt of ammonium platinous chloride and ammonium chloride.

The Action of Silicon on Water below 100°.—H. Moissan and P. Siemens.—If pure amorphous silicon or

powdered silicon crystals are treated with distilled water at 95° in a glass vessel, after six to twelve hours some silicic acid is formed, the water being decomposed. If very thin transparent yellow crystals are used, such as Vigouroux describes (*Ann. de Phys. et de Chim.*, 1897, [7], xii., 64), it may be seen under the microscope that each crystal is coated with a thin layer of the hydrate. The decomposition of water by silicon may also be shown by the following method:—Powdered silicon was placed on the bottom of a glass vessel and distilled water poured on it. A little funnel was immersed with the mouth downwards, the tube being bent downwards and closed. The whole was carefully filled with distilled water, and heated to 95—98° on the water-bath. After some hours, bubbles could be seen on the surface of the silicon. These soon collected in the funnel-tube, and could be shown to consist almost entirely of hydrogen. The analysis of the oxidation product obtained showed that it was silicic acid. The experiment was repeated with different specimens of silicon, and the same result obtained. But if a platinum vessel was used, the water being previously distilled in a platinum retort, no decomposition took place, nor in glass vessels if a trace of fluoric acid was present. On the other hand, the water was decomposed in platinum vessels if distilled water containing a drop of caustic soda or potash or ammonia was used. This behaviour is explained by supposing that the small quantity of alkali in the glass gives rise to the following reactions, the alkaline silicate being decomposed by water forming SiO_2 : $\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} = \text{SiNa}_2\text{O}_3 + 2\text{H}_2$. Thus a very small quantity of alkali can convert a comparatively large quantity of silicon into SiO_2 with evolution of hydrogen.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Artificial Silk.—I should be greatly obliged if any reader could inform me where I can obtain any information on the "alkali-cellulose" process of manufacturing artificial silk. I am practically familiar with the Chardonnet and Lenher methods.—S. Moss.

CHARTERED INSTITUTE OF PATENT AGENTS.

The Qualifying Examination of persons desirous of being registered as Patent Agents will be held in NOVEMBER next. A Notice giving full particulars has appeared in the "Illustrated Official Journal" (Patents) of July 27, 1904, and a copy of such Notice can be obtained on application to the SECRETARY, Chartered Institute of Patent Agents, Staple Inn Buildings, London, W. C.

PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN that

JAMES YATE JOHNSON, of 47, Lincoln's Inn Fields, in the County of London, seeks leave to Amend the Specification of Letters Patent No. 1487 of 1903 granted to him for "Improvements in the Manufacture of Explosives."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents) issued on August 4th, 1904.

Any person, or persons, may give Notice of Opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W. C., within one calendar month from the date of the said Journal.

G. N. DALTON,
Comptroller-General.

JOHNSONS and WILLCOX,
47, Lincoln's Inn Fields, London, W. C.,
Agents for the Applicant.

Young Man (22), Inter. Sc. (Lond.), Registered

Student of Inst. of Chem., thorough training in general Inorganic and Organic, Gas, Water, and Sugar Analysis, desires Post as Junior Chemist in an Analyst's Laboratory. Sound knowledge of Theory, and good references as to ability.—Cecil Wigham, 8, All-farthing Lane, Wandsworth.

UNIVERSITY OF BIRMINGHAM.

SCHOOL OF METALLURGY.

Professor—THOMAS TURNER, M.Sc., A.R.S.M.

Lecturer—O. F. HUDSON, A.R.C.S.

Assistant Lecturer and Demonstrator—GUY RICKETTS,
M.A., A.R.S.M.

A VACATION COURSE IN PRACTICAL METALLURGY will be held at the new METALLURGICAL SMELTING HOUSE, Bournbrook, Birmingham, in SEPTEMBER next. The course will commence on Monday, September 5th, and will last for about six weeks. The regular hours of instruction will be from 9 a.m. to 4 or 5 daily, but attendance may be required at any other time during day or night, as may be found necessary.

For those who already possess some knowledge of Metallurgy, it is believed that the course will afford opportunities which have not hitherto been available in this country.

Fees:—For Students of the University £4 4 0
 External Students (including Entrance Fee). . . £5 5 0

Further particulars may be obtained from the SECRETARY.

THE
DURHAM COLLEGE OF SCIENCE.
 NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided for Students of both sexes proceeding to the University Degrees in Science, or in Letters, and for the University Diploma in Theory and Practice of Teaching. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 26th. Lectures begin October 4th, 1904.
 Prospectuses on application to the SECRETARY.

REDRUTH SCHOOL OF MINES, CORNWALL.

Session 1904-1905 begins September 7th.

A "Mining Certificate" is awarded to Students passing successfully through the School Course. **PRACTICAL MINING CLASSES**, under the instruction of Capt. WILLIAM HAMBY (late Government Inspector, South Africa). Distinctions in Mine Surveying in Open Examination five years in succession, including five Medals and Prizes, being all the awards of the City and Guilds of London Institute in 1904 in this subject. SYLLABUS and every information on application to—
 THE REGISTRAR.

THE CHEMICAL NEWS

AND
 JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 20 words to line)	0	3	6
Each additional line	0	0	6
Whole column	1	15	0
Whole page	3	0	0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
 LONDON, E.C.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

RADIUM

(BROM PUR.)

FROM STOCK

in

1, 2½, & 5 m.g.

Tubes.



ON HIRE,

or at

REASONABLE PRICES.

Pitchblende, from 2/- to 30/- per piece; in Powder, 2/6 per oz.
 Kunzite, (select), 2/- per gramme. Carnotite, 2/- per oz.
 Aeschynit, 2/- per oz.
 Sparteite (See NATURE, March 31, 1904, page 523), 2/- per piece.
 Chlorophane, 2/- per piece. Samarakite, 2/- per oz.
 Zinc Sulphide, green and yellow, 2/6 per tube.
 Rad. Residue, 2/- per tube. Polonium, 21/- per gram; 11/- ½-gram.
 Polonium on Bi rod, 25/- Willemite, 2/- per oz.
 Flexible Sandstone, 3/- to 50/- (See NATURE, June 23, 1904, page 15).

Monazit, 3/- per oz. Monazit Sand, 1/- per oz.
 Diamond chips and powder, 10/- per carat (best quality).
 Euklas, Hiddent, Wagnerit, Phosgenit.
 Bar. Plat. Cyan., for Screens, 3/- gramme, 60/- oz. Crystals, 4/- gramme. Screens, 9d. per square inch.
 Rad.-active Screens, 6d. per square inch. Willemite Screens 6d. per square inch. Electroscopes (special), 21/-.
 Spinthariscopes (special), 21/-, 10/6 and 7/6.
 Selection of Minerals in Boxes, 2/6, 5/6, 10/6 and 21/-.

NEW ZEALAND VEGETABLE CATERPILLAR; from 2 to 3 inches long, with a stem showing fructification growing out of its head. Specimens may be had from 10/6 to 21/-, according to quality and size.

See NATURE, May 12, 1904, page 44.

Goods may be returned if not approved of, when money will be refunded.

Professional Men, Universities, Schools, &c., allowed special terms.

ARMBRECHT, NELSON & CO.

71 & 73, Duke St., Grosvenor Square, W.

E. GEORGE & SONS,
BOOKSELLERS.

161, WHITECHAPEL ROAD, LONDON, E.,

Are OPEN to PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1850, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.

MICA.

Telephone
 No. 2248
 Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., & London.
 102 & 103, Minorities, E.C.,
 MICA MERCHANTS.

Manufacturers of Mica Goods or Electrical and ALL purposes.
 Contractors to His Majesty's Government.

BRYAN CORCORAN Lim.

MILLSTONE BUILDERS,

WIRE WEAVERS, MACHINE MANUFACTURERS AND
 GENERAL MILL FURNISHERS.

Sole Makers of MILBURN'S

Patent Conoidal Stone Grinding Mills.

Especially suitable for certain materials, Wet or Dry.

Works and Warehouses: Back Church Lane,
 Paperi Dept., Basement of the Corn Exchange

31, MARK LANE, LONDON.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.

FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.

LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
 21, Mincing Lane, London, E.C., who hold stock ready for delivery.

THE CHEMICAL NEWS.

VOL. XC., No. 2334.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

CAMBRIDGE, 1904.

INAUGURAL ADDRESS OF THE PRESIDENT,
THE RIGHT HON. A. J. BALFOUR, D.C.L., LL.D., M.P.,
F.R.S., Chancellor of the University of Edinburgh.

Reflections Suggested by the New Theory of Matter.

THE meetings of this great Society have for the most part been held in crowded centres of population, where our surroundings never permit us to forget, were such forgetfulness in any case possible, how close is the tie that binds modern science to modern industry, the abstract researches of the student to the labours of the inventor and the mechanic. This, no doubt, is as it should be. The interdependence of theory and practice cannot be ignored without inflicting injury on both; and he is but a poor friend to either who undervalues their mutual co-operation.

Yet, after all, since the British Association exists for the advancement of science, it is well that now and again we should choose our place of gathering in some spot where science rather than its applications, knowledge, not utility, are the ends to which research is primarily directed.

If this be so, surely no happier selection could have been made than the quiet courts of this ancient University. For here, if anywhere, we tread the classic ground of physical discovery. Here, if anywhere, those who hold that physics is the true *Scientia Scientiarum*, the root of all the sciences which deal with inanimate nature, should feel themselves at home. For, unless I am led astray by too partial an affection for my own University, there is nowhere to be found, in any corner of the world, a spot with which have been connected, either by their training in youth, or by the labours of their maturer years, so many men eminent as the originators of new and fruitful physical conceptions. I say nothing of Bacon, the eloquent prophet of a new era; nor of Darwin, the Copernicus of Biology; for my subject to-day is not the contributions of Cambridge to the general growth of scientific knowledge. I am concerned rather with the illustrious line of physicists who have learned or taught within a few hundred yards of this building—a line stretching from Newton in the seventeenth century, through Cavendish in the eighteenth, through Young, Stokes, Maxwell, in the nineteenth, through Kelvin, who embodies an epoch in himself, down to Rayleigh, Larmor, J. J. Thomson, and the scientific school centred in the Cavendish laboratory, whose physical speculations bid fair to render the closing years of the old century and the opening years of the new as notable as the greatest which have preceded them.

Now what is the task which these men, and their illustrious fellow-labourers out of all lands, have set themselves to accomplish? To what end led these "new and fruitful physical conceptions" to which I have just referred? It is often described as the discovery of the "laws connecting phenomena." But this is certainly a misleading, and in my opinion a very inadequate, account of the subject. To begin with, it is not only inconvenient, but confusing, to describe as "phenomena" things which do not appear, which never have appeared, and which never can appear, to beings so poorly provided as ourselves with the apparatus of sense perception. But apart from this, which is a linguistic error too deeply rooted to be easily exterminated, is it not most inaccurate in sub-

stance to say that a knowledge of Nature's laws is all we seek when investigating Nature? The physicist looks for something more than what, by any stretch of language, can be described as "co-existences" and "sequences" between so-called "phenomena." He seeks for something deeper than the laws connecting possible objects of experience. His object is physical reality; a reality which may or may not be capable of direct perception; a reality which is in any case independent of it; a reality which constitutes the permanent mechanism of that physical universe with which our immediate empirical connection is so slight and so deceptive. That such a reality exists, though philosophers have doubted, is the unalterable faith of science; and were that faith *per impossibile* to perish under the assaults of critical speculation, science, as men of science usually conceive it, would perish likewise.

If this be so, if one of the tasks of science, and more particularly of physics, is to frame a conception of the physical universe in its inner reality, than any attempt to compare the different modes in which, at different epochs of scientific development, this intellectual picture has been drawn, cannot fail to suggest questions of the deepest interest. True, I am precluded from dealing with such of these questions as are purely philosophical by the character of this occasion, and with such of them as are purely scientific by my own incompetence. But some there may be sufficiently near the dividing line to induce the specialists who rule by right on either side of it to view with forgiving eyes any trespasses into their legitimate domain which I may be tempted, during the next few minutes, to commit.

Let me, then, endeavour to compare the outlines of two such pictures, of which the first may be taken to represent the views prevalent towards the end of the eighteenth century; a little more than a hundred years from the publication of Newton's "Principia," and, roughly speaking, about midway between that epoch-making date and the present moment. I suppose that if at that period the average man of science had been asked to sketch his general conception of the physical universe, he would probably have said that it essentially consisted of various sorts of ponderable matter, scattered in different combinations through space, exhibiting most varied aspects under the influence of chemical affinity and temperature, but through every metamorphosis obedient to the laws of motion, always retaining its mass unchanged, and exercising at all distances a force of attraction on other material masses, according to a simple law. To this ponderable matter he would (in spite of Rumford) have probably added the so-called "imponderable" heat, then often ranked among the elements; together with the two "electrical fluids," and the corpuscular emanations supposed to constitute light.

In the universe as thus conceived, the most important forms of action between its constituents was action at a distance; the principle of the conservation of energy was, in any general form, undreamed of; electricity and magnetism, though already the subjects of important investigation, played no great part in the Whole of things; nor was a diffused ether required to complete the machinery of the universe.

Within a few months, however, of the date assigned for these deliverances of our hypothetical physicist, came an addition to this general conception of the world, destined profoundly to modify it. About a hundred years ago Young opened, or re-opened, the great controversy which finally established the undulatory theory of light, and with it a belief in an interstellar medium by which undulations could be conveyed. But this discovery involved much more than the substitution of a theory of light which was consistent with the facts for one which was not; since here was the first authentic introduction into the scientific world-picture of a new and prodigious constituent—a constituent which has altered, and is still altering, the whole

* The hypothesis of an ether was, of course, not new. But before Young and Fresnel it cannot be said to have been established.

balance (so to speak) of the composition. Unending space, thinly strewn with suns and satellites, made or in the making, supplied sufficient material for the mechanism of the heavens as conceived by Laplace. Unending space filled with a continuous medium was a very different affair, and gave promise of strange developments. It could not be supposed that the ether, if its reality were once admitted, existed only to convey through interstellar regions the vibrations which happen to stimulate the optic nerve of man. Invented originally to fulfil this function, to this it could never be confined. And accordingly, as everyone now knows, things which, from the point of view of sense perception, are as distinct as light and radiant heat, and things to which sense perception makes no response, like the electric waves of wireless telegraphy,* intrinsically differ, not in kind, but in magnitude alone.

This, however, is not all, nor nearly all. If we jump over the century which separates 1804 from 1904, and attempt to give in outline the world-picture as it now presents itself to some leaders of contemporary speculation we shall find that in the interval it has been modified, not merely by such far-reaching discoveries as the atomic and molecular composition of ordinary matter, the kinetic theory of gases, and the laws of the conservation and dissipation of energy, but by the more and more important part which electricity and the ether occupy in any representation of ultimate physical reality.

Electricity was no more to the natural philosophers in year 1700 than the hidden cause of an insignificant phenomenon.† It was known, and had long been known, that such things as amber and glass could be made to attract light objects brought into their neighbourhood; yet it was about fifty years before the effects of electricity were perceived in the thunderstorm. It was about 100 years before it was detected in the form of a current. It was about 120 years before it was connected with magnetism; about 170 years before it was connected with light and ethereal radiation.

But to-day there are those who regard gross matter, the matter of everyday experience, as the mere appearance of which electricity is the physical basis; who think that the elementary atom of the chemist, itself far beyond the limits of direct perception, is but a connected system of monads or sub-atoms which are not electrified matter, but are electricity itself; that these systems differ in the number of monads which they contain in their arrangement, and in their motion relative to each other and to the ether; that on these differences, and on these differences alone, depend the various qualities of what have hitherto been regarded as indivisible and elementary atoms; and that while in most cases these atomic systems may maintain their equilibrium for periods which, compared with such astronomical processes as the cooling of a sun, may seem almost eternal, they are not less obedient to the law of change than the everlasting heavens themselves.

But if gross matter be a grouping of atoms, and if atoms be systems of electrical monads, what are these electrical monads? It may be that, as Professor Larmor has suggested, they are but a modification of the universal ether, a modification roughly comparable to a knot in a medium which is inextensible, incompressible, and continuous. But whether this final unification be accepted or not, it is certain that these monads cannot be considered apart from the ether. It is on their interaction with the ether that their qualities depend; and without the ether an electric theory of matter is impossible.

Surely we have here a very extraordinary revolution. Two centuries ago electricity seemed but a scientific toy. It is now thought by many to constitute the reality of which matter is but the sensible expression. It is but a century ago that the title of an ether to a place among the constituents of the universe was authentically established.

It seems possible now that it may be the stuff out of which that universe is wholly built. Nor are the collateral inferences associated with this view of the physical world less surprising. It used, for example, to be thought that mass was an original property of matter, neither capable of explanation nor requiring it; in its nature essentially unchangeable, suffering neither augmentation nor diminution under the stress of any forces to which it could be subjected; unalterably attached to, or identified with, each material fragment, howsoever much that fragment might vary in its appearance, its bulk, its chemical, or its physical condition.

But if the new theories be accepted these views must be revised. Mass is not only explicable, it is actually explained. So far from being an attribute of matter considered in itself, it is due, as I have said, to the relation between the electrical monads of which matter is composed and the ether in which they are bathed. So far from being unchangeable, it changes, when moving at very high speeds, with every change in its velocity.

Perhaps, however, the most impressive alteration in our picture of the universe required by these new theories is to be sought in a different direction. We have all, I suppose, been interested in the generally accepted views as to the origin and development of suns with their dependent planetary systems; and the gradual dissipation of the energy which during this process of concentration has largely taken the form of light and radiant heat. Follow out the theory to its obvious conclusions, and it becomes plain that the stars now visibly incandescent are those in mid-journey between the nebulae from which they sprang and the frozen darkness to which they are predestined. What, then, are we to think of the invisible multitude of the heavenly bodies in which this process has been already completed? According to the ordinary view, we should suppose them to be in a state where all possibilities of internal movement were exhausted. At the temperature of interstellar space their constituent elements would be solid and inert; chemical action and molecular movement would be alike impossible, and their exhausted energy could obtain no replenishment unless they were suddenly rejuvenated by some celestial collision, or travel into other regions warmed by newer suns.

This view must, however, be profoundly modified if we accept the electric theory of matter. We can then no longer hold that if the internal energy of a sun were as far as possible converted into heat either by its contraction under the stress of gravitation or by chemical reactions between its elements, or by any other inter-atomic force; and that, were the heat so generated to be dissipated, as in time it must be, through infinite space, its whole energy would be exhausted. On the contrary, the amount thus lost would be absolutely insignificant compared with what remained stored up within the separate atoms. The system in its corporate capacity would become bankrupt—the wealth of its individual constituents would be scarcely diminished. They would lie side by side, without movement, without chemical affinity; yet each one, howsoever inert in its external relations, the theatre of violent motions, and of powerful internal forces.

Or, put the same thought in another form. When the sudden appearance of some new star in the telescopic field gives notice to the astronomer that he, and perhaps, in the whole universe, he alone, is witnessing the conflagration of a world, the tremendous forces by which this far-off tragedy is being accomplished must surely move his awe. Yet not only would the members of each separate atomic system pursue their relative course unchanged, while the atoms themselves were thus riven violently apart in flaming vapour, but the forces by which such a world is shattered are really negligible compared with those by which each atom of it is held together.

In common, therefore, with all other living things, we seem to be practically concerned chiefly with the feeble forces of Nature, and with energy in its least powerful manifestations. Chemical affinity and cohesion are on this

* First known through the theoretical work of Maxwell and the experiments of Herz.

† The modern history of electricity begins with Gilbert, but I have throughout confined my observations to the post-Newtonian period.

theory no more than the slight residual effects of the internal electrical forces which keep the atom in being. Gravitation, though it be the shaping force which concentrates nebulae into organised systems of suns and satellites, is trifling compared with the attractions and repulsions with which we are familiar between electrically charged bodies; while these again sink into insignificance beside the attractions and repulsions between the electric monads themselves. The irregular molecular movements which constitute heat, on which the very possibility of organic life seems absolutely to hang, and in whose transformations applied science is at present so largely concerned, cannot rival the kinetic energy stored within the molecules themselves. This prodigious mechanism seems outside the range of our immediate interests. We live, so to speak, merely on its fringe. It has for us no promise of utilitarian value. It will not drive our mills; we cannot harness it to our trains. Yet not less on that account does it stir the intellectual imagination. The starry heavens have from time immemorial moved the worship or the wonder of mankind. But if the dust beneath our feet be indeed compounded of innumerable systems, whose elements are ever in the most rapid motion, yet retain through uncounted ages their equilibrium unshaken, we can hardly deny that the marvels we directly see are not more worthy of admiration than those which recent discoveries have enabled us dimly to surmise.

Now, whether the main outlines of the world-picture which I have just imperfectly presented to you be destined to survive, or whether in their turn they are to be obliterated by some new drawing on the scientific palimpsest, all will, I think, admit that so bold an attempt to unify physical nature excites feelings of the most acute intellectual gratification. The satisfaction it gives is almost aesthetic in its intensity and quality. We feel the same sort of pleasurable shock as when from the crest of some melancholy pass we first see far below us the sudden glories of plain, river, and mountain. Whether this vehement sentiment in favour of a simple universe has any theoretical justification I will not venture to pronounce. There is no *a priori* reason that I know of for expecting that the material world should be a modification of a single medium, rather than a composite structure built out of sixty or seventy elementary substances, eternal and eternally different. Why, then, should we feel content with the first hypothesis and not with the second? Yet so it is. Men of science have always been restive under the multiplication of entities. They have eagerly noted any sign that the chemical atom was composite, and that the different chemical elements had a common origin. Nor, for my part, do I think such instincts should be ignored. John Mill, if I rightly remember, was contemptuous of those who saw any difficulty in accepting the doctrine of "action at a distance." So far as observation and experiment can tell us, bodies do actually influence each other at a distance. And why should they not? Why seek to go behind experience in obedience to some *a priori* sentiment for which no argument can be adduced? So reasoned Mill, and to his reasoning I have no reply. Nevertheless, we cannot forget that it was to Faraday's obstinate disbelief in "action at a distance" that we owe some of the crucial discoveries on which both our electric industries and the electric theory of matter are ultimately founded; while at this very moment physicists, however baffled in the quest for an explanation of gravity, refuse altogether to content themselves with the belief, so satisfying to Mill, that it is a simple and inexplicable property of masses acting on each other across space.

These obscure intimations about the nature of reality deserve, I think, more attention than has yet been given to them. That they exist is certain; that they modify the indifferent impartiality of pure empiricism can hardly be denied. The common notion that he who would search out the secrets of Nature must humbly wait on experience, obedient to its slightest hint, is but partly true. This may be his ordinary attitude; but now and again it happens that

observation and experiment are not treated as guides to be meekly followed, but as witnesses to be broken down in cross-examination. Their plain message is disbelieved, and the investigating judge does not pause until a confession in harmony with his preconceived ideas has, if possible, been wrung from their reluctant evidence.

This proceeding needs neither explanation nor defence in those cases where there is an apparent contradiction between the utterances of experience in different connections. Such contradictions must of course be reconciled, and science cannot rest until the reconciliation is effected. The difficulty really arises when experience apparently says one thing and scientific instinct persists in saying another. Two such cases I have already mentioned; others will easily be found by those who care to seek. What is the origin of this instinct, and what its value; whether it be a mere prejudice to be brushed aside, or a clue which no wise man would disdain to follow, I cannot now discuss. For other questions there are, not new, yet raised in an acute form by these most modern views of matter, on which I would ask your indulgent attention for yet a few moments.

That these new views diverge violently from those suggested by ordinary observation is plain enough. No scientific education is likely to make us, in our unreflective moments, regard the solid earth on which we stand, or the organised bodies with which our terrestrial fate is so intimately bound up, as consisting wholly of electric monads very sparsely scattered through the spaces which these fragments of matter are, by a violent metaphor, described as "occupying." Not less plain is it that an almost equal divergence is to be found between these new theories and that modification of the common-sense view of matter with which science has in the main been content to work.

What was this modification of common sense? It is roughly indicated by an old philosophic distinction drawn between what were called the "primary" and the "secondary" qualities of matter. The primary qualities, such as shape and mass, were supposed to possess an existence quite independent of the observer; and so far the theory agreed with common sense. The secondary qualities, on the other hand, such as warmth and colour, were thought to have no such independent existence, being, indeed, no more than the results due to the action of the primary qualities on our organs of sense-perception; and here, no doubt, common sense and theory parted company.

You need not fear that I am going to drag you into the controversies with which this theory is historically connected. They have left abiding traces on more than one system of philosophy. They are not yet solved. In the course of them the very possibility of an independent physical universe has seemed to melt away under the solvent powers of critical analysis. But with all this I am not now concerned. I do not propose to ask what proof we have that an external world exists, or how, if it does exist, we are able to obtain cognisance of it. These may be questions very proper to be asked by philosophy; but they are not proper questions to be asked by science. For, logically, they are antecedent to science, and we must reject the sceptical answers to both of them before physical science becomes possible at all. My present purpose requires me to do no more than observe that, be this theory of the primary and secondary qualities of matter good or bad, it is the one on which science has in the main proceeded. It was with matter thus conceived that Newton experimented. To it he applied his laws of motion; of it he predicated universal gravitation. Nor was the case greatly altered when science became as much pre-occupied with the movements of molecules as it was with those of planets. For molecules and atoms, whatever else might be said of them, were at least pieces of matter, and, like other pieces of matter, possessed those "primary" qualities supposed to be characteristic of all matter, whether found in large masses or in small.

But the electric theory which we have been considering

carries us into a new region altogether. It does not confine itself to accounting for the secondary qualities by the primary, or the behaviour of matter in bulk by the behaviour of matter in atoms; it analyses matter, whether molar or molecular, into something which is not matter at all. The atom is now no more than the relatively vast theatre of operations in which minute monads perform their orderly evolutions; while the monads themselves are not regarded as units of matter, but as units of electricity; so that matter is not merely explained, but is explained away.

Now the point to which I desire to call attention is not to be sought in the great divergence between matter as thus conceived by the physicist and matter as the ordinary man supposes himself to know it, between matter as it is perceived and matter as it really is, but to the fact that the first of these two quite inconsistent views is wholly based on the second.

This is surely something of a paradox. We claim to found all our scientific opinions on experience; and the experience on which we found our theories of the physical universe is our *sense-perception* of that universe. That is experience; and in this region of belief there is no other. Yet the conclusions which thus profess to be entirely founded upon experience are to all appearance fundamentally opposed to it; our knowledge of reality is based upon illusion, and the very conceptions we use in describing it to others, or in thinking of it ourselves, are abstracted from anthropomorphic fancies, which science forbids us to believe and Nature compels us to employ.

We here touch the fringe of a series of problems with which inductive logic ought to deal, but which that most unsatisfactory branch of philosophy has systematically ignored. This is no fault of men of science. They are occupied in the task of making discoveries, not in that of analysing the fundamental presuppositions which the very possibility of making discoveries implies. Neither is it the fault of transcendental metaphysicians. Their speculations flourish on a different level of thought; their interest in a philosophy of nature is lukewarm; and howsoever the questions in which they are chiefly concerned be answered, it is by no means certain that the answers will leave the humbler difficulties at which I have hinted either nearer to or further from a solution. But though men of science and idealists stand acquitted, the same can hardly be said of empirical philosophers. So far from solving the problem, they seem scarcely to have understood that there was a problem to be solved. Led astray by a misconception to which I have already referred; believing that science was concerned only with (so-called) "phenomena," that it had done all that it could be asked to do if it accounted for the sequence of our individual sensations, that it was concerned only with the "laws of Nature," and not with the inner character of physical reality; disbelieving, indeed, that any such physical reality does in truth exist;—it has never felt called upon seriously to consider what are the actual methods by which science attains its results, and how those methods are to be justified. If anyone, for example, will take up Mill's logic, with its "sequences and co-existences between phenomena," its "method of difference," its "method of agreement," and the rest; if he will then compare the actual doctrines of science with this version of the mode in which those doctrines have been arrived at,—he will soon be convinced of the exceedingly thin intellectual fare which has been hitherto served out to us under the imposing title of Inductive Theory.

There is an added emphasis given to these reflections by a train of thought which has long interested me, though I acknowledge that it never seems to have interested anyone else. Observe, then, that in order of logic sense-perceptions supply the premisses from which we draw all our knowledge of the physical world. It is they which tell us there is a physical world; it is on their authority that we learn its character. But in order of causation they are effects due (in part) to the constitution of our organs of sense. What we see depends not merely on what there is to be seen, but

on our eyes. What we hear depends not merely on what there is to hear, but on our ears. Now, eyes and ears, and all the mechanism of perception, have, as we know, been evolved in us and our brute progenitors by the slow operation of Natural Selection. And what is true of sense-perception is of course also true of the intellectual powers which enable us to erect upon the frail and narrow platform which sense-perception provides, the proud fabric of the sciences.

Now Natural Selection only works through utility. It encourages aptitudes useful to their possessor or his species in the struggle for existence, and, for a similar reason, it is apt to discourage useless aptitudes, however interesting they may be from other points of view, because, being useless, they are probably burdensome.

But it is certain that our powers of sense-perception and of calculation were fully developed ages before they were effectively employed in searching out the secrets of physical reality—for our discoveries in this field are the triumphs but of yesterday. The blind forces of Natural Selection, which so admirably simulate design when they are providing for a present need, possess no power of prevision, and could never, except by accident, have endowed mankind, while in the making, with a physiological or mental outfit adapted to the higher physical investigations. So far as natural science can tell us, every quality of sense or intellect which does not help us to fight, to eat, and to bring up children, is but a by-product of the qualities which do. Our organs of sense-perception were not given us for purposes of research; nor was it to aid us in meting out the heavens or dividing the atom that our powers of calculation and analysis were evolved from the rudimentary instincts of the animal.

It is presumably due to these circumstances that the beliefs of all mankind about the material surroundings in which it dwells are not only imperfect, but fundamentally wrong. It may seem singular that down to, say, five years ago, our race has, without exception, lived and died in a world of illusions; and that its illusions, or those with which we are here alone concerned, have not been about things remote or abstract, things transcendental or divine, but about what men see and handle, about those "plain matters of fact" among which common sense daily moves with its most confident step and most self-satisfied smile. Presumably, however, this is either because too direct a vision of physical reality was a hindrance, not a help, in the struggle for existence; because falsehood was more useful than truth; or else because with so imperfect a material as living tissue no better results could be attained. But, if this conclusion be accepted, its consequences extend to other organs of knowledge besides those of perception. Not merely the senses, but the intellect, must be judged by it; and it is hard to see why evolution, which has so lamentably failed to produce trustworthy instruments for obtaining the raw material of experience, should be credited with a larger measure of success in its provision of the physiological arrangements which condition reason in its endeavours to turn experience to account.

Considerations like these, unless I have compressed them beyond the limits of intelligibility, do undoubtedly suggest a certain inevitable incoherence in any general scheme of thought which is built out of materials provided by natural science alone. Extend the boundaries of knowledge as you may; draw how you will the picture of the universe; reduce its infinite variety to the modes of a single space-filling ether; retrace its history to the birth of existing atoms; show how under the pressure of gravitation they became concentrated into nebulae, into suns, and all the host of heaven; how, at least in one small planet, they combined to form organic compounds; how organic compounds became living things; how living things, developing along many different lines, gave birth at last to one superior race; how from this race arose, after many ages, a learned handful, who looked round on the world which thus blindly brought them into being, and judged it, and knew it for what it was:—perform, I say, all this, and, though you

may indeed have attained to science, in nowise will you have attained to a self-sufficing system of beliefs. One thing at least will remain, of which this long-drawn sequence of causes and effects gives no satisfying explanation; and that is knowledge itself. Natural science must ever regard knowledge as the product of irrational conditions, for in the last resort it knows no others. It must always regard knowledge as rational, or else science itself disappears. In addition, therefore, to the difficulty of extracting from experience beliefs which experience contradicts, we are confronted with the difficulty of harmonising the pedigree of our beliefs with their title to authority. The more successful we are in explaining their origin, the more doubt we cast on their validity. The more imposing seems the scheme of what we know, the more difficult it is to discover by what ultimate criteria we claim to know it.

Here, however, we touch the frontier beyond which physical science possesses no jurisdiction. If the obscure and difficult region which lies beyond is to be surveyed and made accessible, philosophy, not science, must undertake the task. It is no business of this Society. We meet here to promote the cause of knowledge in one of its great divisions; we shall not help it by confusing the limits which usefully separate one division from another. It may perhaps be thought that I have disregarded my own precept—that I have wilfully overstepped the ample bounds within which the searchers into Nature carry on their labours. If it be so I can only beg your forgiveness. My first desire has been to rouse in those who, like myself, are no specialists in physics, the same absorbing interest which I feel in what is surely the most far-reaching speculation about the physical universe which has ever claimed experimental support; and if in so doing I have been tempted to hint my own personal opinion that as natural science grows it leans more, not less, upon an idealistic interpretation of the universe, even those who least agree may perhaps be prepared to pardon.

ON THE RELATION BETWEEN THE SPECTRA OF SUNSPOTS AND STARS.*

By Sir NORMAN LOCKYER, K.C.B., LL.D., F.R.S.

As the period throughout which the observations of widened lines have been made at South Kensington now includes two maxima and three minima epochs of solar activity, it has seemed desirable to discuss the results obtained, taking into account the chemical origins of the lines affected in passing from the photosphere to the sunspot nuclei. This is going on, but in anticipation of its publication, I desire to direct attention to one of the conclusions arrived at in its bearing upon the question of the temperature conditions of the Arcturian and lower type stars, which formed part of the subject of a recent paper (*Proc. Roy. Soc.*, 1904, vol. lxxiii., pp. 227-238).

Since 1894, when the last discussion of the widened line results was published (*Proc. Roy. Soc.*, 1894, vol. lvii., p. 199), nearly 10,500 observations of lines in sunspot spectra have been made at South Kensington. An analysis of these lines, in respect to their origins, shows that the elements chiefly affected during the period 1892-1903, inclusive, were vanadium and titanium.

The great importance of vanadium and titanium in sunspot spectra has also been demonstrated by Father Corty during his observations in the B-D region at Stonyhurst (*Monthly Notices, R.A.S.*, June, 1903, vol. lxi., No. 8, pp. 479-480).

It was foreshadowed in a previous paper on the chemical classification of the stars (*Proc. Roy. Soc.*, 1899, vol. lxx., p. 191) that it seemed probable that, as the result of further work, the "genera" then proposed might have to be split

up into "species." During the more recent research mentioned above the temperature classification was tested by comparing the relative intensities of the red and ultra-violet ends of the spectra of stars, situated on various horizons of the temperature curve, including Capella and Arcturus, which, according to the original general classification, belong to the same type, viz., "Arcturian." It was found that the spectrum of Capella extended on an average about 70 tenth-metres further into the ultra-violet than that of Arcturus, whilst the red portion of the spectrum is certainly stronger in the latter. That is to say, the general temperature of Arcturus is probably appreciably lower than that of Capella.

The next step was to see if chemical change accompanied this reduction of temperature, and if so, whether the change was in any way related to the change from the photosphere to the sunspot spectrum.

In comparing, for this purpose, the spectra taken with a 6-inch Henry prismatic camera it was noticed that certain lines were relatively intensified in passing from the spectrum of Capella to that of Arcturus.

Similar comparisons of the Fraunhofer spectrum with the spectra of Capella and Arcturus respectively were next made. This worked led to the following conclusions:—(1) That the line absorptions of Capella and the sun are practically identical; (2) that although, speaking generally, the same lines occur in the spectra of the sun and Arcturus, yet in the latter many lines are relatively more intense than in the former. Moreover, in the great majority of such cases the lines so intensified are probably due to vanadium and titanium.

Thus we see that whilst the temperature classification mentioned above certainly places Arcturus on a lower temperature level than Capella, and therefore the sun, the evidence obtained from a study of the line absorptions of Arcturus and of sunspots indicates very clearly that the temperature of the Arcturian absorbing atmosphere is about the same as that of the sunspot nuclei during the above-mentioned period.

This conclusion justifies the ideas formulated by De la Rue, Stewart, and Loewy, that the spots are produced by the downrush of cooler material.

In a recent publication ("The Spectra of Stars of Secchi's Fourth Type," "The Decennial Publications," Chicago University, 1903), which has been received here since the above-mentioned comparisons were completed, Professor Hale suggests that because the lines which are widened in sunspots appear as strong dark lines in Piscian stars, the effect may be produced because sunspots are more numerous in such stars. From the evidence adduced above it seems a far more probable explanation to suppose that these lines are intensified in sunspots, and strengthened in those stars which have been placed on lower temperature levels than the sun, because the general temperature conditions are similar. That is to say, the fall of temperature experienced by the metallic vapours in passing from the photosphere to the spot nucleus is of the same order as that to which an absorbing atmosphere is subjected in passing from the temperature conditions of Capella or the sun to that of Arcturus or the lower temperature stars.

Determination of Palladium.—H. Erdmann and O. Makowka.—The use of acetylene for the determination of palladium and its separation from other metals offers many advantages over that of hydrazine, as described by Jannasch recently. By means of this reagent palladium is readily separated from platinum, iridium, rhodium, and gold. For, by addition of acetylene either in aqueous solution or as a gas to the strongly acid solution in the cold, the palladium separates out in the form of a yellowish brown precipitate readily soluble in ammonia. This precipitate is not explosive, and on ignition with a small quantity of ammonium nitrate in a current of hydrogen readily yields the pure metal. The presence of copper does not hinder the reaction, as is the case when hydrazine is used.—*Berichte*, xxxvii., No. 11.

* A Paper read before the Royal Society, June 16, 1904.

THE
SEPARATION OF THE MOST VOLATILE GASES
FROM AIR WITHOUT LIQUEFACTION.*

By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S.,
Jacksonian Professor, University of Cambridge, and
Fullerian, Royal Institution, London.

FROM the time when liquid air came to be an ordinary laboratory agent I have continually used it for the purpose of producing high vacua in vessels that had been previously filled with easily condensable gases, like sulphurous acid, carbonic acid, vapour of water, or benzol.

When the liquefaction of hydrogen was effected, one of the first scientific uses to which it was put was that described in my paper on the "Application of Liquid Hydrogen to the Production of High Vacua, together with their Spectroscopic Examination" (*Proc. Roy. Soc.*, 1898, vol. lxiv.; *CHEMICAL NEWS*, vol. lxxix., p. 73). In that communication it was shown by theory and confirmed by experiment that the condensing power of liquid hydrogen is so great relatively to that of liquid oxygen or nitrogen, that any closed vessel a part of which is cooled to the boiling-point of hydrogen must suddenly become a highly vacuous space. This was proved by the great difficulty of getting electric discharges to pass through specially prepared spectroscopic tubes when subjected to liquid hydrogen cooling, and from the fact that when the current did pass no lines of oxygen or nitrogen were seen, but only those of hydrogen, helium, and neon. In order to separate these latter gases from air, it was necessary to liquefy a quantity of air and to distil off the most volatile portion at as low a temperature as possible into a separate receiver placed in liquid hydrogen. In this way many spectroscopic tubes were filled with the uncondensable air gases, and the results of their examination is recorded in a paper entitled "On the Spectra of the More Volatile Gases of Atmospheric Air, which are not Condensed at the Temperature of Liquid Hydrogen," by Professor Liveing and myself (*Proc. Roy. Soc.*, 1900, vol. lxxvii.; *CHEMICAL NEWS*, vol. lxxxiii., p. 1).

Some two years later I improved the method of separation of the volatile air gases. The process is fully described and illustrated in my paper on "Problems of the Atmosphere" (*Proc. Roy. Inst.*, 1902). Its success depends upon the continuous direct liquefaction of air at atmospheric pressure combined with a device which enables the more volatile gases to be trapped and separated. In this way some 1/35,000th of the volume of the air liquefied is collected as a gaseous mixture having the composition 38 per cent of nitrogen, 4 per cent of hydrogen, and 58 per cent of mixed helium and neon. After sparking to remove the nitrogen and hydrogen, a gaseous mixture of helium and neon, containing a little argon, was obtained. This mixture had the composition of 16 per cent helium and 84 per cent neon. In both methods of treatment it will be noted the liquefaction of the air was the essential preliminary operation, to be supplemented in the one case by the use of liquid hydrogen, in the other by sparking to remove the nitrogen. The paper already communicated to the Royal Society, entitled "The Absorption and Thermal Evolution of Gases Occluded in Charcoal at Low Temperatures," in which the greatly increased power of occlusion possessed by charcoal at low temperatures is proved, suggested an inquiry into the limits of gaseous pressure reached by such means of condensation. (See *CHEMICAL NEWS*, vol. xc., p. 73).

With this object a narrow tube *CE*, Fig. 1, was sealed to an ordinary spectroscopic sparking tube *AB*, at the end

E an enlarged space was blown out capable of holding a few grammes of coconut charcoal. After the charcoal had been freed from gases by heating and exhaustion, and the poles cleared by sparking during this operation, pure and dry gases like oxygen, nitrogen, air, carbonic oxide, hydrogen, neon, and helium could be admitted at different pressures, and the tube with its charcoal chamber attached sealed off.

On placing the charcoal end of the apparatus in liquid air the gas in each case was rapidly absorbed, and the vacuum produced reached the phosphorescent stage in all cases with the exception of hydrogen, neon, and helium. A small Crookes's radiometer, full of air at atmospheric pressure, with charcoal tube attached, became quite active to heat radiation when the charcoal was cooled for half a minute in liquid air. To test the amount of exhaustion reached by the use of a given weight of coconut charcoal, I sealed on a tube containing 30 grms. to a large electric discharge tube of 1300 c.c. capacity filled with air at atmospheric pressure. On cooling the charcoal receptacle in liquid air the pressure diminished to 50 m.m. of mercury. Repeating the same experiment, but starting with the tube initially at half an atmosphere, the exhaustion reached was now beyond the striæ stage. A further experiment, starting with one-fourth of an atmosphere, gave a vacuum through which no discharge passed.

Finally, the 30 grms. of charcoal were replaced by only 1 grm., and the initial pressure was reduced to 3 m.m. of mercury. Now the vacuum just reached the beginning of the phosphorescent stage. With hydrogen, either a pressure of gas less than that of the atmosphere had to be used at starting, or a larger amount of charcoal employed in order to get a vacuum well up in the striæ stage. If, however, the liquid air was cooled to -210°C . by exhaustion, the tube just reached the beginning of phosphorescence round the cathodes.

With helium there was a very slight absorption, but neon did show something more appreciably. Spectroscopic observations made during the condensation of the gas in the charcoal showed the gradual disappearance of the characteristic spectrum of oxygen, nitrogen, and air, as the high vacuum was reached and the discharge passed with great difficulty. In tubes of this kind filled at atmospheric pressure I could always see the F line of hydrogen and the neon yellow; but the helium was not seen with any definiteness. As the amount of neon in the air cannot well exceed 1/50,000th, the spectroscopic test is very delicate.

In order to bring in the helium lines it was necessary to concentrate the volume of air in the space of the sparking tube six or seven times. This was done by the use of an arrangement shown in Fig. 2. *AB* is the sparking tube with its small charcoal bulb *C* attached, capable of being sealed off when required at *G*; and *D* and *E* are larger charcoal absorbers placed in vacuum tubes containing liquid air; the whole being attached to a graduated gas-holder containing air. A series of glass stopcocks are attached at the points *h*, *i*, *j*, and *k* in order to facilitate manipulation. In determining the volume of air required to bring in the helium lines, only one charcoal absorber containing about 15 grms. of material was used. On allowing 200 c.c. of air from the gas-holder to be sucked into the charcoal (which had been previously exhausted along with the sparking tube), on opening the stopcock *h* any residuary gas in *D* was swept into the sparking tube, which was then sealed off at *G*.

This tube gave the hydrogen lines *C* and *F*, the neon yellow, and some of the orange lines, along with the helium yellow and green, quite distinct. With the residuary gas extracted from 1 litre of air I could see all the helium lines. On the positive pole the neon yellow and the green of helium were alone marked, while the negative pole gave both the neon and helium yellow lines along with the helium green and the F of hydrogen on the continuous spectrum. From this it would appear that the spectroscopic test for helium is as delicate as that for neon, and that

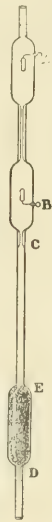


FIG. 1.

* A Paper read before the Royal Society, June 16, 1904.

1/50,000th can be recognised. From 3 litres of air discharge tubes were obtained, giving the neon and helium spectra associated with a brilliant ruddy glow discharge.

efficient assistance in the conduct of the experiments, and Mr. J. W. Heath, F.C.S., has also helped me in the investigation.

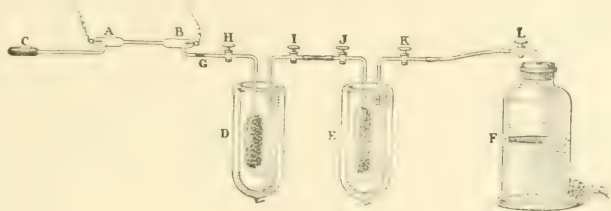


FIG. 2.

As 40–50 grms. of charcoal can absorb at the temperature of liquid air from 5–6 litres, it is easy to accumulate rapidly the uncondensed gases in considerable quantities for spectroscopic examination. For this purpose I found it convenient to use two charcoal condensers in circuit, as represented in Fig. 2. After the charcoal in the first one marked E was saturated, the stopcock K was closed, while I and J were opened for a short time, so as to allow the less condensable gas in E to be sucked into the second vessel of the same type D along with some portion of air. The charcoal condenser E was then taken out of the liquid air, and rapidly heated to 15° C. in order to expel the occluded air. It was thus in a condition to repeat the absorption. In this way 50 litres of air can be treated in a short time. Sparking tubes filled from the accumulated gases in D were very brilliant, showing the complete spectrum of the volatile constituents of air. It is hardly necessary to remark that after the little charcoal receptacle connected to each of the sparking tubes had been cooled, and thus all traces of air absorbed, it can be sealed off, leaving the spectroscopic tubes intact. The complete spectroscopic study of the products must be left for further examination with Professor Living.

The method I have described will be equally applicable to the treatment of the gaseous products from minerals containing helium, hydrogen, &c., and also to the radium products of a similar kind. It seems even probable that the separation of the less volatile constituents in air may be improved by a slight modification in the mode of working. The behaviour of the gases from the Bath Springs has been examined. When the gas containing 1/1000th part of helium in what may be regarded as pure nitrogen is subjected to charcoal absorption exactly in the same way as the air was treated, no high vacuum is reached. All the nitrogen and any other constituents disappear, and a spectrum of helium and hydrogen showing much less neon than exists in the volatile residue from atmospheric air is the result. A sample of argon made from Bath gas gave, when the argon was absorbed in charcoal, a gas residuum giving the helium and neon spectrum, and the same result follows the use of atmospheric argon. In the case, however, of the Bath gas argon the helium spectrum is the stronger, whereas with air argon the neon is the most pronounced.

In order to further test the method, the crude gases got by heating the mineral Fergussonite were examined. During the cooling of the charcoal the nitrogen and hydrogen spectra were marked, but in a short time nothing could be seen but the lines of hydrogen and helium.

Great interest will attach to the behaviour of helium, hydrogen, and the most volatile part of air when subjected to the action of charcoal cooled to the temperature of liquid hydrogen. The method promises to open up many avenues for future inquiry.

I am indebted to Mr. Robert Lennox, F.C.S., for

THE USE OF TETROXALATE OF POTASSIUM IN TITRATION.

IN 1856, Krant proposed using tetroxalate of potassium for titrations, but the proposition was received with very varying opinions on the part of analytical chemists. Some looked upon the tetroxalate as a substance which could be obtained easily as a definite chemical compound; that is to say, in a pure state and of constant weight; others, on the other hand, did not admit this characteristic, and did not consider that it was suitable for making titrations. More especially Meinecke's assertion was rejected as incorrect, according to which tetroxalate of potassium dried for some weeks over concentrated sulphuric acid, could be obtained pure and would have the following composition:— $C_2O_4.HK + C_2O_4.H_2 + 2H_2O$.

According to a paper of O. Kuhling's (*Zeit. f. Ang. Chem.*, 1903, p. 1030), he has succeeded in preparing this salt in the pure state. He proposes to use the following method:—

By Cl. Winkler's method, commercial oxalic acid is crystallised twice in warm hydrochloric acid of 1.07 density, and three times in boiling distilled water. The product obtained should not contain any of the halogen elements, and should not leave any residue on calcination. It is placed in a quantity of water insufficient to dissolve it for twenty-four to forty-eight hours. It is then transferred to a glass flask and shaken frequently. A quarter of this cold saturated solution is taken and treated according to Meinecke's method with a few drops of phenolphthalein, and, while stirring, a solution of potassic hydrate, freshly prepared and crystallised in alcohol, is poured in up to the moment when a persistent red colouration appears. The neutralised solution is then treated with the remaining three-quarters of the tetroxalate solution, the sides of the glass are rubbed with a glass stirring rod, and soon we observe the formation of a crystalline deposit of tetroxalate of potassium. To obtain the best results it is necessary to re-dissolve the crystals first formed in the mother-liquor by heating it to the required temperature; the vessel is then placed in cold water, and the sides of the glass again rubbed with a glass rod to effect the re-crystallisation of the tetroxalate. To have a perfectly pure salt, the powder obtained is drained on a hard filter, re-dissolved, and re-crystallised two or three times, treating it with smaller and smaller quantities of boiling distilled water, and cooling rapidly after each heating. The product, drained as before, and protected from the action of dust, is dried between sheets of filter-paper until a small portion pressed against the surface of a dry glass does not show any trace of moisture; this generally takes about two days. The salt is then kept in well-stoppered bottles.

From the numerous experiments made by the author and the values he has obtained in the titrations effected, he

attributes the following formula to the salt prepared by the above method: $\text{—C}_2\text{O}_4\text{HK} + \text{C}_2\text{O}_4\text{H}_2 + 2\text{H}_2\text{O}$.

The author also finds that this salt keeps very well.—*Pharmac. Centralblatt.*, vol. xlv., p. 915.

RADIO-ACTIVE LEAD, RADIO-TELLURIUM, AND POLONIUM.

By A. DEBIERNE.

POLONIUM, which was first discovered by M. and Mme. Curie, has the following characteristic properties:—Its solutions are precipitated by hydrogen sulphide in presence of an acid, and it resembles bismuth in various chemical reactions. Its radiation is distinct from that of uranium, thorium, radium, and actinium, and consists entirely of the almost non-penetrating α -rays, which are only slightly affected by a magnet. Polonium gives out no emanations, and does not induce radio-activity.

Two other radio-active substances, which are also precipitated by hydrogen sulphide, have been found in pitchblende. MM. Hofmann and Strauss first called attention to a chemically active substance analogous to lead, which is known as radio-active lead, whilst M. Marckwald published several papers dealing with another active body known as radio-tellurium, which is obtained with polonium and retained by tellurium in several reactions. Mme. Curie and M. Giesel question the existence of this latter body, which they consider to be identical with polonium.

Having at my disposal a large quantity of the residues left from the extraction of radium, I tried to obtain MM. Hofmann and Strauss' substance. The lead contained in these residues was first dissolved in strong soda solution, then precipitated by sodium sulphide in the form of sulphide. The sulphides were then transformed into nitrates, evaporated to dryness, and re-dissolved in water, and purified as completely as possible by a number of crystallisations from water.

These nitrates had a very slight radio-activity, only twice that of uranium. By force of circumstances these were kept for three years before being worked again, and during this period the radio-activity remained constant. Various efforts to concentrate the activity by fractional crystallisation were made on the radio-active lead thus obtained.

The crystallisation of the nitrates is of very little use, that of the chloride or the acetate giving decidedly better results. However, the most advantageous method consists in adding a large excess of hydrochloric acid to a hot concentrated solution of the nitrate. Under these conditions a large proportion of the lead chloride precipitates or crystallises out on cooling, and nearly all the radio-activity remains in the solution. This solution is concentrated and more hydrochloric acid added, whereby more lead chloride is deposited. By repeating these operations several times the non-active lead chloride can be eliminated, and the greater part of the activity can be concentrated in a small quantity of matter. This portion, which contains chiefly lead, is purified from small traces of copper and iron, and then transformed into nitrate. The solution is next concentrated, made slightly acid, and added to a large quantity of water. A very slight precipitate of basic bismuth nitrate is formed.

This precipitate contains nearly all the radio-activity, and possesses all the characteristics of poloniferous bismuth. Its activity is extremely great; it has not been measured exactly, but is certainly more than 100,000 times as great as that of uranium. The radiation has similar properties to that of polonium; it forms a homogenous pencil of almost non-penetrating rays, which are only slightly affected by the magnetic field. The active matter thus obtained also shows all the properties of the radio-tellurium of M. Marckwald. It gives with stannous chloride a slight very active precipitate, and a thin piece of bismuth plunged in a hydrochloric solution of this substance

becomes covered with a slight deposit of extremely radio-active matter.

It is thus seen that the same radio-active substance shows successively properties characteristic of radio-active lead, polonium, and radio-tellurium. The apparent conclusion to be drawn is that there is no distinction between these three bodies, and that in pitchblende there only exists a single radio-active substance which is precipitated by sulphuretted hydrogen in acid solution. The name polonium should naturally be the one retained, as that was originally given by M. and Mme. Curie.

We can also conclude from the above experiments that a radio-active substance cannot be identified by chemical reactions, and on account of the very small quantities contained in minerals, analytical separations merely cause this substance to be shared amongst the different fractions.

One test only can be employed with certainty, and this is the nature of the radio-activity and the identity of the radiation emitted by polonium, radio-tellurium, and radio-active lead would in itself predict the results obtained above.

I will conclude this paper by drawing attention to the fact that the radio-active lead nitrate which was used in these researches has absolutely retained its activity for several years, although it was so feeble; whilst in the specimens of polonium obtained during the first experiments this activity gradually disappeared. The constancy of the activity must then depend on external conditions which it will be very important to determine. It is possible that under certain conditions the activity of other substances, such as uranium, thorium, radium, and actinium, will diminish and disappear in the same manner as that of polonium.—*Comptes Rendus*, vol. cxxxix., No. 4, p. 283.

PRELIMINARY NOTES UPON SANSEVIERA THYRSIFLORA.

By FREDERICK DAVIS.

The plant *Sansevieria thyrsiflora*, indigenous to South Africa, belongs to the natural order *Liliaceae*, and is largely used in its fresh state as a remedy for piles. Many other species of the same family, such as *Sansevieria zeylanica*, are the source of a very strong and tough fibre known commercially as "bow-string hemp." It was noticed during the African campaign that Boers suffering from hemorrhoids dug up a portion of the rhizome, freed it from extraneous matter, trimmed off the outer integuments, and chewed the inner portion, swallowed the extractives, and rejected the fibres which remained as a tangled mass in the mouth after chewing.

Captain Tremlett observing this ascertained that in each case a cure was effected, and desiring to know more of the remedy a quantity of the rhizome was sent to an English consulting physician, who directed me to ascertain the best methods of preserving the extractives without impairing the physiological action, and if possible determine the active constituents.

There is practically no literature upon the subject, but I notice in Prof. Andrew Smith's "Contributions to the South African Materia Medica" the following remarks:—"This plant is to be seen frequently beneath trees and in thickets, with its sword-shaped leathery leaves with a border and zig-zag white markings. Its root is given by Dr. Pappe as used for piles. The Kaffirs employ a decoction of the root-stock to expel all kinds of worms. An experienced native declares it to be very efficacious."

The plant is known in Africa as Sikolakota, and by the Kaffirs as "Isi kolakota."

My researches seem to prove the rhizome contains:—

1. A glucoside.
2. A globulin.
3. An albumen.

The globulin and the albumen reside principally in the plexm of the fibro-vascular bundles, whilst the glucoside is found chiefly in the inner portion of the outer integument and the ground tissue; it will be imperative, therefore, in making any extract or other preparation from this plant that the whole rhizome be employed, or the entire medicinal constituents will not be obtained.

Secondly, I am of opinion that any medicinal preparation of this plant should be made from the fresh rhizome, because, if partially dried, fermentation would be set up, with the consequent decomposition of the active principles, and its efficacy as a medicament would be destroyed, whilst the entirely dried rhizome, although free from the objection of enzymotic change, is found to be less active for the purpose for which it is intended, and in addition, if not dried quickly and at a low temperature, its colour suffers markedly.

The best preparation pharmaceutically, and most active physiologically, has been made by the following simple method:—

Press out the juice from the fresh rhizome, filter, and preserve by the addition of 20 per cent of glycerin.

The addition of ethylic alcohol impairs the physiological action.

The character of the glucoside found somewhat resembles that of glycyrrhizin; from ultimate analysis it is probably identical, $C_{44}H_{63}NO_{18}$.

The substance is optically inactive, and several separately obtained samples varied in melting-point between 178° and 200° .

It must be distinctly understood the above preliminary statement does not profess to be the exhaustive results, as indications have already been obtained of the presence of another important constituent.

NOTES ON THE SOFTENING OF HARD WATER.

By NICHOLAS KNIGHT.

THE work was done in the Chemical Laboratory of Cornell College by C. G. Eldredge.

A water, which is probably a fair type of the various supplies in the dolomite region of the Mississippi Valley, was studied with a view to rendering it more soft for domestic and boiler purposes. The water supply of Mount Vernon, in Eastern Iowa, was examined. The water is pumped from a well 330 feet in depth, of which 315 feet is in the Niagara magnesian limestone. The substances, therefore, which cause the hardness are calcium and magnesium carbonates, with a small amount of calcium sulphate.

The total amount of the solids in the water was obtained by evaporating 500 c.c. to dryness in a weighed platinum evaporating dish of 150 c.c. capacity, and afterwards drying in an air-bath at 110° to constant weight. From this the silica, iron and alumina, calcium and magnesium were determined. The amounts of sulphates and alkaline chlorides were estimated from other portions of water. On account of a possible variation in the quantity of dissolved substances in such waters, the entire amount required for these experiments was taken at the same time and kept in a cool place in glass-stoppered bottles. The numbers given express the amounts of the various substances in 100,000 parts of the water.

1. Total solids in platinum dish	28.86
$CaCO_3$	12.47
$MgCO_3$	10.42
$CaSO_4$	0.989
SiO_2	2.12
Fe_2O_3 and Al_2O_3	0.266
NaCl and KCl	2.34
	28.60

A. The Effect of Boiling on Precipitating the Calcium and Magnesium Carbonates.

2. Five hundred c.c. of the water was placed in a litre flask of Jena glass, heated to boiling with a triple burner, and boiled vigorously for two minutes. Ten c.c. of the water evaporated by the boiling. The flask was allowed to cool, the contents were filtered, and the filtrate evaporated to dryness in the platinum dish, and treated in every respect like the unboiled specimen. The amounts obtained were as follows:—

Total solids in platinum dish	23.38
$CaCO_3$	9.27
$MgCO_3$	9.53
$CaSO_4$	0.98
SiO_2	1.68
Fe_2O_3 and Al_2O_3	0.25
NaCl and KCl	2.34
	24.05

The difference between the results here obtained and in No. 1 is due chiefly to the precipitation of calcium carbonate. The magnesium suffered a comparatively slight change. The boiling water in this and subsequent experiments did not seem to dissolve the glass, as shown by the amount of silica obtained.

3. Five hundred c.c. of the water was heated to boiling in the flask, and the boiling was vigorously continued for ten minutes. Forty-five c.c. of the water evaporated during the time. The total solids obtained in the platinum dish = 20.00.

$CaCO_3$	4.92
$MgCO_3$	9.75
$CaSO_4$	0.98
SiO_2	1.78
Fe_2O_3 and Al_2O_3	0.32
NaCl and KCl	2.34
	20.09

4. Five hundred c.c. boiled for twenty minutes in the same flask; 70 c.c. evaporated. The filtered residue, evaporated to dryness in the platinum dish, gave as the total solids 19.18.

$CaCO_3$	4.25
$MgCO_3$	8.52
$CaSO_4$	0.98
SiO_2	1.66
Fe_2O_3 and Al_2O_3	0.27
NaCl and KCl	2.34
	18.62

Boiling twenty minutes removes about 66 per cent of the calcium carbonate and 18 per cent of the magnesium carbonate—about 44 per cent of the temporary hardness. It should also be noted that where the hardness is more largely due to calcium and magnesium sulphates, with smaller amounts of the carbonates, boiling to remove the carbonates would tend to increase the concentration of the solution of sulphates, and therefore the hardness of the water, instead of diminishing, might be increased.

B. The Effect of Lime-water on the Calcium and Magnesium Carbonates.

Three hundred c.c. of the water was shaken in a flask with 150 c.c. of lime-water. The mixture was allowed to stand twenty-four hours, when it was filtered and evaporated to dryness. The total solids were found to be 15.10.

All of the magnesium carbonate was removed, but an excess of calcium oxide from the lime-water remained. The experiment was repeated a number of times to find the minimum of lime-water that would leave the smallest quantity of total solids. The lime-water was prepared from distilled water. The following proportions were used:—

112½ c.c. of lime-water to 300 c.c. of the water.

75	"	"	"
100	"	"	"
37½	"	"	"
90	"	"	"
30	"	"	"
22½	"	"	"

In each case the total solids obtained were comparatively large, either from the excess of lime-water used or because the amount of lime-water was insufficient to remove the carbonates to any extent. The experiments were repeated with baryta-water, but the results were also unsatisfactory. In a number of trials it was sought to remove the excess of lime by acidifying the mixture with a stream of carbon dioxide. On evaporation the carbon dioxide would escape, and the solution would again react alkaline. In other cases the mixture of the water and lime-water was allowed to stand in a shallow dish exposed to the air for a number of days, and then filtered and evaporated. No attempt was made to remove the excess of calcium oxide with sodium carbonate.

A more satisfactory result was obtained by taking 300 c.c. of the water, and using two or three drops of a tenth normal solution of silver nitrate as an indicator. The lime-water was dropped from a burette until the mixture showed an alkaline reaction. Fifty c.c. of lime-water was required.

Total solids	15.14
CaCO ₃	5.21
MgCO ₃	4.23
CaSO ₄	0.98
SiO ₂	2.12
Fe ₂ O ₃ and Al ₂ O ₃	0.26
NaCl and KCl	2.34
	15.14

The experiment was repeated, using as an indicator two or three drops of phenolphthalein solution made by dissolving 1 gm. of the powder in 200 c.c. of 95 per cent alcohol. Fifty c.c. of lime-water was again required. The result is as follows:—

CaCO ₃	2.41
MgCO ₃	4.13
CaSO ₄	0.98
SiO ₂	2.12
Fe ₂ O ₃ and Al ₂ O ₃	0.26
NaCl and KCl	2.34

12.24

The best results seem to come from adding the lime-water to the water in the ratio of one to six. The lime-water can be tasted in the mixture, which is quite unfit for drinking purposes. This of course would not be an objection for boiler use.

Chemical Laboratory, Cornell College,
July 12, 1904.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxvii., No. 11, 1904.

Atomic Weight of Iodine.—P. Köthner and E. Aeuer.

—Two years ago Ladenberg described a new method of preparing pure iodine, depending upon the different solubilities of the silver haloid salts in ammonia; and with the iodine thus obtained he carried out atomic weight determinations, finding, as the mean of three experiments, $I = 126.960$ ($O = 16$). The value found by Stas, using three different methods, is 126.85, and both these numbers have been confirmed by other observers—the one by Scott, and he other by Marignac. The authors undertook a particularly exhaustive and careful research to explain this

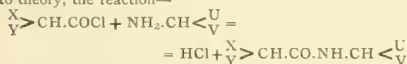
difference and establish the true atomic weight. They found that Ladenburg's method, resting on the determination of the ratio of AgI to $AgCl$ by decomposition of AgI in a current of chlorine, was liable to error, but not sufficient to account for the difference between his and Stas' number. Using the same method, and taking all precautions, they found, as the mean of eight experiments, that the atomic weight is 126.936. However, using a different specimen of silver iodide, which was as pure as Stas' preparation, they obtained a value practically identical with his. Hence they concluded that the treatment of silver iodide with ammonia really purified it, and elaborated another method of obtaining perfectly pure iodine, viz., the distillation of ethyl iodide, which boils at 72°, while ethyl chloride boils at 12°, and the bromide at 38°. The pure ethyl iodide was carefully fractionated, and the hydrogen iodide obtained from it was precipitated with a weighed quantity of silver. This synthesis gave $I = 125.978$. Finally, they synthesised silver iodide by igniting silver in a current of iodine—a method which undoubtedly gives the lowest limit of the atomic weight. This gave 126.963 (vacuum). Thus the authors believe that they may safely say definitely that the atomic weight of iodine is not less than 126.963.

Solubility of Silicon in Silver, and a Modification of Silicon Soluble in Hydrofluoric Acid.—H. Moissan and F. Siemens.—Silicon is much more soluble in silver than in lead or zinc, and begins to dissolve at 960°. On allowing the silicon to crystallise out from the solution, part of it is found to differ from other forms of silicon in that it is soluble in hydrofluoric acid. The solubility of silicon in silver rises decidedly with the temperature, and the percentage of silicon soluble in hydrofluoric acid decreases as the total amount of silicon dissolved increases. Moreover, it was found that more of the soluble silicon dissolves if the silver is not saturated with silicon, and if only 2 per cent of silicon is contained in the silver, practically all the silicon which crystallises out is soluble in hydrogen fluoride. The crystals of this new modification of silicon are mostly thin, yellow, transparent scales, their size depending on the rate of crystallisation. Their density in water and benzene very nearly approximates to that of the other forms of silicon. When heated to 1200° in a current of hydrogen or nitrogen, this modification still retains its solubility in hydrofluoric acid. Careful analysis proved the absence in it of all impurities except traces of iron and microscopic crystals of carborundum. It is to be noted that the preparation of this modification must be performed in a reducing atmosphere, since otherwise the silver absorbs the oxygen present, which then oxidises a portion of the silicon, and thus a mixture of silicon and silica is obtained.

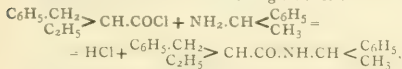
Products of Decomposition of Brom-succinic Acid and its Salts in Aqueous Solution.—Wolf Johannes Müller and F. Suckert.—On heating dilute solutions of brom-succinic acid malic acid is chiefly formed, while in concentrated solutions fumaric acid is the principal product. Fumaric and malic acids only differ from one another by one molecule of water. The authors found that by titrating a completely decomposed solution of brom-succinic acid the total amount of organic acids was given, which could be calculated to fumaric salt. On evaporating the solution and weighing the residue the actual quantity of salt was obtained, the difference giving the extra water which the malic acid contains, from which the amount of malic acid can be calculated. Applying this method at different temperatures, they found that the amount of fumaric acid formed is proportional to the concentration of the brom succinic acid raised to the power 3/2, and that raising the temperature increases the formation of fumaric acid. On the other hand, salts of brom-succinic acid give rise to pure malic acid only, no trace of fumaric acid being formed. The addition of hydrochloric acid increases the proportion of fumaric acid, independently of the temperature, and this increase is greater in dilute than in concentrated solutions of brom-succinic acid.

Fluorescence.—Hugo Kauffmann and Alfred Beisswenger.—3-Aminophthalimide shows a green fluorescence and yellow colour in dissociating media, such as water and alcohol, and a violet fluorescence and a paler yellow colour in benzene and ligroin and other non-dissociating media. This change in colour and fluorescence in different solvents has been supposed to be due to tautomerism. Further research, however, has shown that it is due to changes in the benzene ring. The authors have now proved that (1) the change of fluorescence is by no means limited to 3-aminophthalimide and its derivatives, but is a general property of fluorescing amines. Moreover, the change in colour is a property of non-fluorescing amines. Temperature has some influence on fluorescence and colour; for example, a solution of acridone in pyridine has in the cold a violet fluorescence, which almost completely disappears on heating; (2) the fluorescence and colour changes cannot be due to tautomerism, for the introduction of amyl and alkyl groups, *i.e.*, the prevention of the possibility of such tautomerism, does not abolish the change of fluorescence; (3) the molecular weights of some amines were determined in benzene by the cryoscopic method, and it was shown that the molecular weight in non-dissociating solvents is the simplest. By their experiments the authors have proved that the changes do not depend upon a change of molecular weight. There was still the possibility that compounds were formed between the dissolved substance and the solvent. But such compounds can hardly be concerned in the fluorescence and colour changes, as both strongly and feebly basic amines, which, moreover, can be formed from most different classes of compounds, behave in exactly the same manner.

Proof of Racemic Character.—E. Mohr.—According to theory, the reaction—



should give a mixture of two structurally identical stereoisomeric racemic acid amides; and this reaction could, under suitable conditions, be applied to determine whether an amide or acid chloride is racemic or not. The author has examined the case of the following reaction:—



and found that the product could be very readily split into two constituents by systematic crystallisation from boiling petroleum ether; these two substances melted at 112° and 85°—87° respectively, and analysis showed that their formula was C₁₉H₂₃ON. Thus, by means of this reaction (or a similar one), it can be experimentally determined whether a substance is a racemic compound (or an inactive mixture) or not, without actually decomposing it into its two optically active components (or isolating one of them), and without the aid of optically active substances. Van't Hoff has already suggested a method for proving the racemic nature of a compound without directly splitting it up, but he employed an optically active substance.

Decomposition of Paracautchouc by means of Ozone.—C. Harries.—Paracautchouc is remarkably stable towards permanganate. The author has shown by a number of experiments that unsaturated compounds, when treated with ozone, can attack the molecule O₃ at each double bond. The resulting explosive ozonides are decomposed on warming with water into aldehydes or ketones and hydrogen peroxide. Pure paracautchouc is attacked much less easily than the vulcanised substance, but if the caoutchouc is dissolved in chloroform and then treated with ozone, on removal of the chloroform a colourless syrup remains (*viscous*) which behaves like an ozonide. It may be purified by dissolving in acetic ether and precipitating with petroleum ether. Analysis of the purified substance points to the formula C₁₀H₁₆O₆. The molecular

weight is about 526, but the ozonide thus prepared still contains some chlorine, owing to the difficulty of completely removing the chloroform. When boiled with water for a short time the aqueous solution gives the very characteristic reactions of the keto- and di-aldehydes, laevulinic aldehyde, and succinic aldehyde. If the boiling with water is allowed to proceed for a longer time, the hydrogen peroxide evolved oxidises the aldehyde first formed to the corresponding acids, laevulinic acid and a small quantity of an acid allied to, but not identical with succinic acid. The formation of laevulinic acid shows that the simple molecule C₁₀H₁₆ must contain the complex radical $\begin{array}{c} \text{C} \\ \text{C} \end{array} > \text{C}:\text{CH}.\text{CH}_2.\text{CH}_2.\text{C}:\text{CH}.\text{C}$. It is noteworthy

that no trace of oxalic acid results, while oxidation of caoutchouc and its derivatives by other means produces large quantities of it. The ozonides possess the property of emitting rays which appear to act on the photographic plate much more strongly than ozone; this property is possessed in a high degree by the caoutchouc ozonide here described.

Chromates of the Polyatomic Metals.—O. Meyer.—*Chromates of Silver.*—The precipitation of a solution of NO₃Ag by means of Cr₂O₇K₂ with or without the addition of an excess of nitric acid, always gives the dichromate, Cr₂O₇Ag₂, a ruby-red powder which dissolves when heated in the presence of an excess of nitric acid, and re-crystallises on cooling into very fine plates resembling iodine. The trichromate is never obtained. The dichromate is soluble in the cold in 12,000 parts of water. *Dichromate of Barium.*—This salt, Cr₂O₇Ba, forms in crystals resembling dichromate of potassium both in form and colour, when the neutral chromate of barium is treated with an excess of CrO₃; it crystallises on cooling, in clinorhombic prisms. Pure water decomposes it into CrO₃+CrO₃Ba; it is unattacked, however, by glacial acetic acid even when heated; we can thus wash the crystals. *Chromates of Lead.*—When we endeavour to prepare Cr₂O₇Pb we generally obtain a mixture of the neutral salt with a little acid salt (PbCl₂ with CrO₃ in boiling solution, or acetate of lead, CrO₃ and NO₂H). However, we can obtain pure Cr₂O₇Pb in a reddish-brown crystalline powder from acetate of lead, CrO₃ and NO₂H of r₄ density, by boiling them for several hours in a flask fitted with a vertical condenser.—*Berichte*, vol. xxxvi., p. 1740.

Experiments with the Emanation from Bromide of Radium.—In some experiments carried out with the object of showing the dispersion of the emanation of bromide of radium, M. Th. Indricson (*Journ. de la Soc. Phys. Chim. R.*, vol. xxxvi., p. 7) made use of a long tube, the inner surface of which was covered with a layer of Sidot's blende (sulphide of zinc). After having put it into communication with a test-tube containing a solution of bromide of radium (10 m.m. in 10 c.c.), we observe a luminescence appear and travel along the tube. By repeating Ramsay's experiment, the author observed that the yellow line of helium did not correspond exactly with the two yellow lines in the spectrum of the emanation; in fact, it was placed between these two latter. After having plunged the serpentine tube communicating with the test-tube into liquid air, the author observed in the spectrum of the emanation a reinforcement of the lines corresponding to the helium lines, and between the two yellow lines already mentioned appeared a third line corresponding exactly with the yellow line of helium. The helium lines do not exist in the spectrum of the emanation in a recently prepared tube, but only appear after a time. On examining the gases set free during the solution of the bromide of radium, the author observed that the helium lines did not exist as long as the tube remained phosphorescent in the dark. When after four days this phosphorescence had disappeared, the helium lines were observed in the spectrum.—*Revue Generale des Sciences*, 15th Year, No. 13, July 15, 1904.

THE VICTORIA UNIVERSITY OF MANCHESTER. CHEMICAL COURSE.

Full particulars of this Course, qualifying for the UNIVERSITY DEGREES IN CHEMISTRY and the Technological Chemistry Certificate, will be forwarded on application to the REGISTRAR.

The SESSION commences on OCTOBER 4th.

THE DURHAM COLLEGE OF SCIENCE NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided for Students of both sexes proceeding to the University Degrees in Science, or in Letters, and for the University Diploma in Theory and Practice of Teaching. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 26th. Lectures begin October 4th, 1904.

Prospectuses on application to the SECRETARY.

THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

DEPARTMENTS OF CHEMISTRY, TECHNICAL CHEMISTRY, and METALLURGY.

Chemistry	Prof. G. G. HENDERSON, M.A., D.Sc., F.I.C.
Technical Chemistry	Prof. THOMAS GRAY, D.Sc., Ph.D.
Metallurgy	Prof. A. HUMBOLDT SEXTON, F.C.S., F.I.C.

The Courses of Instruction in these Departments are arranged for Students preparing to become Manufacturing or Analytical Chemists, Metallurgists, or Science Teachers. The courses in Chemistry qualify for the Examinations of the Institute of Chemistry and of the Universities of Glasgow, Edinburgh, and London.

SESSION 1904-5 begins on TUESDAY, SEPTEMBER 27th; the ENTRANCE EXAMINATION begins on MONDAY, SEPTEMBER 19th.

CALENDAR (by post 1s. 4d.), containing regulations for the Associateship of the College, may be obtained from the SECRETARY, 38, Bath Street, Glasgow. PROSPECTUS free.

QUEEN'S COLLEGE, GALWAY.

The MATRICULATION EXAMINATION of SESSION 1904-1905 commences on OCTOBER 21st. Matriculation Certificates of any University within the United Kingdom are accepted.

All Lectures, Scholarships, Exhibitions, and Prizes are Open to Students of either sex.

The Scholarship Examinations in Arts, Medicine, and Engineering commence on OCTOBER 20th.

DEPARTMENTS OF SCIENCE, MEDICINE, & ENGINEERING.

Mathematics	Prof. THOMAS JOHN L'ANSON BROWNHILL, M.A., Fellow of St. John's College, Cambridge; Examiner, R.U.I.
Physics	Prof. A. ANDERSON, M.A. (Camb.), Hon. LL.D. (Glasgow), late Fellow of Sidney Sussex College, Cambridge, Member of the Senate of the Royal University of Ireland, President of the College.
Chemistry	Prof. ALFRED SENIER, Ph.D., Berlin.
Natural History, Mineralogy, and Geology	Prof. RICHARD J. ANDERSON, M.A., M.D., M.R.C.S., Eng.; Examiner, R.U.I.
Engineering	Prof. EDWARD TOWNSEND, M.A., D.Sc.; Examiner, R.U.I.
Anatomy and Physiology	Prof. JOSEPH P. FEE, M.D., M.Ch., D.Sc., F.R.U.I.
Practice of Medicine	Prof. JOHN ISAAC LYNHAM, M.D., M.Ch., M.A.O., F.R.U.I.
Surgery	Prof. W. W. BERRINGTON, F.R.C.S.I., M.R.C.P.
Materia Medica	Prof. NICHOLAS W. COLOHAN, M.D., M.Ch.
Gynaecology	Prof. RICHARD J. KINKADE, B.A., M.D., L.R.C.S.I.

Prospectus of the Courses and Regulations for Scholarships, &c., can be had on application to the—

REGISTRAR,
Queen's College, Galway.

TEXT-BOOKS OF PHYSICAL CHEMISTRY. Edited by Sir WILLIAM RAMSAY, K.C.B., F.R.S. NEW VOLUME JUST PUBLISHED.

"Collectively the manuals will form an adequate record of the present state of knowledge in a large and important field of chemistry. We heartily wish well to Sir William Ramsay's venture, and look with interest for the appearance of the succeeding numbers of the series."
—GLASGOW HERALD.

ELECTRO-CHEMISTRY. Part I.—GENERAL THEORY.

By R. A. LEHFELDT, D.Sc.,

Professor of Physics at the East London Technical College.

Including a Chapter on the Relation of Chemical Constitution to Conductivity, by T. S. MOORE, B.A., B.Sc., Lecturer in the University of Birmingham.
Crown 8vo. 5s.

PART II.—Applications to Electrolysis, Primary and Secondary Batteries, &c. [In preparation.]

The Phase Rule and its Applications. By ALEX. FINDLAY, M.A., Ph.D., D.Sc., Lecturer and Demonstrator in Chemistry, University of Birmingham. With 115 Figures in the Text, and an INTRODUCTION TO THE STUDY OF PHYSICAL CHEMISTRY by Sir WILLIAM RAMSAY, K.C.B., F.R.S. Crown 8vo. 5s.

* Sir William Ramsay's "Introduction to Physical Chemistry" is also issued separately, 1s. net.

LONGMANS, GREEN, & CO., 39, Paternoster Row, London, E.C.

CITY OF LONDON COLLEGE,

WHITE STREET and ROPEMAKER STREET,
MOOKFIELDS, E.C.

MICHAELMAS TERM commences OCTOBER 3rd.

CLASSES and LABORATORY WORK in
CHEMISTRY, PHYSICS, BIOLOGY, BOTANY, GEOLOGY, and PHYSIOLOGY. Special preparation for the Examinations of the Pharmaceutical Society, The Conjoint Board. Complete Courses for University Matriculation and Inter, and Final B.Sc., meeting during the Evening and on Saturday.

Full particulars gratis on application to—

DAVID SAVAGE, Secretary.

RADIUM

(BROM. PUR.)

FROM STOCK

in

1, 2, & 5 m.g.

Tubes.

ON HIRE,

or at

REASONABLE

PRICES.



Pitchblende, from 2/- to 30/- per piece; in Powder, 2/6 per oz.
Kunzite, selected, 2/- per gramme. Carnotite, 2/- per oz.
Aeschylite, 2/- per oz.
Spartite (see NATURE, March 31, 1904, page 523), 2/- per piece.
Chlorophane, 2/- per piece. Samarskite, 3/- per oz.
Zinc Sulphide, green and yellow, 2/6 per tube.
Rad. Residue, 2/- per tube. Polonium, 21/- per gram; 11/- 1/2 gram.
Polonium on Bl. rod, 25/- Willemite, 2/- per oz.
Flexible Sandstone, 3/- to 50/-. (See NATURE, June 23, 1904, page 185.)
Monazit, 3/- per oz. Monazit Sand, 1/- per oz.
Diamond chips and powder, 10/- per carat (best quality).
Eukias, Hiddenit, Wagnerit, Phosgenit.
Bar. Plat. Cyan., for Screens, 3/- gramme, 60/- oz. Crystals, 4/- gramme. Screens, 9d. per square inch.
Radio-active Screens, 6d. per square inch. Willemite Screens 6d. per square inch. Electroscopes (special), 21/-.
Sphinterascopes (special), 21/-, 10/6 and 7/6.
Selection of Minerals in Boxes, 9/6, 5/6, 10/6 and 21/-.

NEW ZEALAND VEGETABLE CATERPILLAR: from 2 to 3 inches long, with stem showing fructification growing out of its head. Specimens may be had from 10/6 to 21/-, according to quality and size.

See NATURE, May 12, 1904, page 44.

Goods may be returned if not approved of, when money will be refunded.
Professional Men, Universities, Schools, &c., allowed special terms.

ARMBRECHT, NELSON & CO.

71 & 73, Duke St., Grosvenor Square, W.

THE CHEMICAL NEWS.

VOL. XC., No. 2335.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

CAMBRIDGE, 1904.

By Professor SYDNEY YOUNG, D.Sc., F.R.S.
President of the Section.

THE researches of Hermann Kopp on the molecular volumes and boiling-points of chemical compounds extended over half a century, beginning with his inaugural dissertation on the densities of oxides in 1838, and concluding in 1889 with a review of the whole of the work done on the subject. In his second paper Kopp considered the molecular volumes of solid compounds, and arrived at the conclusion that truly isomorphous substances have the same atomic or molecular volume, but that in other cases the volumes are usually different. Schröder also made the same observation at about the same time.

Now, isomorphous substances have analogous chemical formulae, and are usually of similar chemical character, and it is interesting to notice that at this early date the fact was recognised that close chemical relationship is associated with similarity in physical properties.

For about the first six years Kopp was engaged in the consideration of the results obtained by other observers, and from these results he deduced the most important of his generalisations.

As regards boiling-points, Kopp, in 1842, concluded that a constant difference in chemical composition is accompanied by a constant difference in boiling-point, and he adopted the value 18° as the rise due to the replacement of the methyl by the ethyl group in organic compounds, although the observed differences varied between 11° and 24° . Two years later he found in sixteen comparisons differences varying from 8° to 33° ; but he doubted the correctness of the extreme values, and took 19° as the true value; he further suggested that this is the constant difference for an addition of CH_2 in any homologous series, and he pointed out that the observed difference was most regular in the case of the fatty acids.

Kopp was also of opinion that isomeric compounds with the same composition and the same vapour density have the same boiling-point.

The paucity of experimental data and the wide discrepancies between the results obtained by different observers induced Kopp to undertake the determination of the boiling-points of various compounds, and, later, their molecular volumes at a series of temperatures, and it is interesting to note the comparative crudeness of his first attempts and the increasing attention which he paid to the purification of his compounds and to the elimination of thermometric and other errors. He first examined three pairs of esters in order to find whether isomeric compounds have really the same boiling-points. But he employed only calcium chloride as a dehydrating agent, and this would remove neither water nor the alcohol completely; he was much troubled by the "bumping" of the liquids, and the temperatures he actually observed—with the thermometer bulb in the liquid—fluctuated considerably, and he could only, in most cases, take the lowest temperature observed as the most probable boiling-point. By so doing, and by making a fairly liberal allowance for residual errors, Kopp arrived at the erroneous conclusion that the boiling-points of isomers were the same in the three cases examined, and therefore, probably, in all cases.

The boiling-point of methyl alcohol was of great interest to Kopp, because, taking that of ethyl alcohol—about

which there was general agreement—as correct, it should, according to his law, be $78^\circ - 19^\circ = 59^\circ$, while the temperatures actually observed varied from 60° to 66° . Kopp prepared a specimen of methyl alcohol, and found that it boiled at about 65° ; but he had more faith in his law than in his experimental result, and he concluded that the methods of determining boiling-points were not sufficiently accurate to give results correct to within even 1° or 2° .

In 1854, he discussed the corrections which should be applied to thermometer readings, giving a table of corrections for the unheated column of mercury, and adopting the value 27 m.m. per degree as the value of dp/dt for all substances, in order to reduce the observed boiling-point to that at normal pressure. He pointed out, also, that the height of the barometer should be reduced to 0°C . Taking advantage of Delft's improved method of preparing and purifying methyl alcohol, Kopp made a fresh specimen from methyl oxalate and dried it with lime; but while Delft observed the boiling-point to be 60° , Kopp obtained the value $65.2^\circ - 65.8^\circ$. He was still, however, inclined to think that, owing to bumping, the observed boiling-point was too high, and that the true temperature should be about 60° .

Meanwhile, in 1847, Kopp had examined sixteen liquids, including water, two alcohols, three fatty acids, and seven esters, and in 1854, as a result of his further determinations, he was able to compare the boiling-points—and also the molecular volumes—of a large number of substances, most of which were either alcohols, acids, or esters, and he at first adhered to his previous value of 19° for the rise of boiling-point due to the addition of CH_2 . Later in the same year, however, taking a wider survey and including hydrocarbons and their halogen derivatives, ethers, sulphides, and other compounds, he was obliged to admit that the difference is in some cases higher, in others lower, than 19° , but he still regarded these cases merely as exceptions to the law. In 1867, Kopp admitted that isomeric aromatic hydrocarbons have not always the same boiling-point, and that the difference for an addition of CH_2 was not always 19° ; but he still believed that the difference for CH_2 was constant in any really homologous series—for example, 20.5° for homologues of toluene, 18.5° for those of xylene, and 16.5° for those of trimethylbenzene. He also recognised the fact that isomeric alcohols have widely different boiling-points.

Kopp published no later papers on the boiling-points of organic compounds, although he dealt fully with the question of molecular volumes in his final communication in 1889.

As a pioneer, Kopp had very great difficulties to contend against when he began his researches; data were scanty and far from accurate, and the substances which could be most easily obtained, and, it was thought, readily purified, were, unfortunately, those which were the least likely to lead to normal generalisations. Water, the alcohols, and the organic acids all contain a hydroxyl group, and we now know that the physical properties of these substances are abnormal in nearly all respects, owing probably to the fact that their molecules tend to associate together; moreover, the esters, which are formed by the interaction of acids and alcohols, do not behave quite normally, and there is probably molecular association, though to a much smaller extent than with the hydroxyl compounds.

There can be little doubt that if Kopp had been able, in the first place, to obtain a considerable number of pure substances of normal behaviour, such as the paraffins or their halogen derivatives, he would not have been led to the erroneous conclusions which he defended with such vigour for so many years. If we take the normal paraffins as the simplest class of organic compounds, we find that, instead of the boiling-points rising by equal intervals as the series is ascended, the rise, which is very large for the lowest numbers, becomes smaller and smaller as the molecular weight increases. This fact is, of course, now well known, and various formulæ have been suggested to reproduce these boiling-points. Thus, Walker has proposed the formula $T = aM^b$, where T is the boiling-point on

the absolute scale of temperature, M is the molecular weight, and a and b are constants. Ramage has this year suggested that this formula applies only to the CH_2 chain linkage, and that the influence of the terminal hydrogen atoms is considerable in the case of the lowest members, but diminishes as the chain lengthens, and becomes eventually either constant or negligible. In other words, the lower members of the series cannot be regarded as truly homologous, and that is a point which is, I think, important to bear in mind. Ramage suggests a new formula, $T = n[M(1 - 2^{-n})] + 1$, where n is Walker's constant, 37.3775, and n is the number of carbon atoms in the molecule. He assumes, however, a constant difference for CH_2 in the case of the alcohols, the aldehydes, and the ketones, but I doubt whether the boiling-points of the last two classes of compounds are yet sufficiently well established to allow of any certain conclusions being drawn from them.

I am inclined to think that it may be useful to regard the value of Δ (the rise of boiling-point for an increment of CH_2) as being mainly a function of the absolute temperature, and I would provisionally suggest the formula $\Delta = \frac{144.86}{T^{0.0148}}$, where Δ is the difference between the boiling-point, T , of any paraffin, and that of its next higher homologue. Taking the boiling-point of methane as $106.75^\circ \text{ abs.}$, the values for the higher members agree better with the observed temperatures than those given by Ramage's formula, as will be seen by Table I.

TABLE I.
Boiling-point (abs. temp.)

Paraffin.	Observed.	Calculated. Ramage.	Δ .	Calculated. Young.	Δ .
CH_4	108.3	105.7	- 2.6	106.75	+ 1.55
C_2H_6	180.0	177.3	- 2.7	177.7	- 2.3
C_3H_8	228.0	231.9	+ 3.9	229.85	+ 1.85
C_4H_{10}	274.0	275.6	+ 1.6	272.6	- 1.4
C_5H_{12}	309.3	312.2	+ 2.9	309.4	+ 0.1
C_6H_{14}	341.95	343.9	+ 1.95	341.95	0
C_7H_{16}	371.4	374.3	+ 0.9	371.3	- 0.1
C_8H_{18}	398.6	398.3	- 0.3	398.1	- 0.5
C_9H_{20}	422.5	422.5	0	422.85	+ 0.35
$\text{C}_{10}\text{H}_{22}$	446.0	445.2	- 0.8	445.85	- 0.15
$\text{C}_{11}\text{H}_{24}$	467.0	466.8	- 0.2	467.35	+ 0.35
$\text{C}_{12}\text{H}_{26}$	487.5	487.3	- 0.2	487.65	+ 0.15
$\text{C}_{13}\text{H}_{28}$	507.0	507.0	0	506.8	- 0.2
$\text{C}_{14}\text{H}_{30}$	525.5	526.0	+ 0.5	525.0	- 0.5
$\text{C}_{15}\text{H}_{32}$	543.5	544.2	+ 0.7	542.3	- 1.2
$\text{C}_{16}\text{H}_{34}$	560.5	561.9	+ 1.4	558.85	- 1.65
$\text{C}_{17}\text{H}_{36}$	576.0	579.0	+ 3.0	574.7	- 1.3
$\text{C}_{18}\text{H}_{38}$	590.0	595.7	+ 5.7	589.9	- 0.1
$\text{C}_{19}\text{H}_{40}$	603.0	611.9	+ 8.9	604.5	+ 1.5

I do not wish, however, to lay much stress on the actual form of the equation, or on the particular values of the constants; the chief point I wish to call attention to is that Δ may be regarded as a function of the temperature.

Suppose that we replace a terminal atom of hydrogen in each normal paraffin by chlorine, so as to form the homologous series of primary alkyl chlorides. The boiling-points of these chlorides are much higher, and the differences, Δ , are much smaller than for the corresponding paraffins, but the gradual fall in the values of Δ as the series is ascended is unmistakable. The same remarks apply to the bromides and iodides, the boiling-points being still higher and the values of Δ smaller.

But the point of chief interest appears to me to be this: If the values of Δ for the halogen derivatives are plotted against the absolute temperatures, the points for the most part fall near the curve constructed for the paraffins, and represented by the formula $\Delta = \frac{144.86}{T^{0.0148}}$. The first value

of Δ is decidedly low in each case (average deviation from curve 2.7°); the later ones are rather high in nearly every case (average deviation 0.86°). Similar results are in

general obtained with other homologous series of compounds in which molecular association is not believed to occur, but, as will be seen from Table II., the deviations from the normal paraffin curve are greater in the case of those series the lower members of which, according to Ramsay and Shields, are characterised by molecular association.

In the great majority of cases the deviations are greatest for the lowest members of a series, the calculated values of Δ being almost invariably higher than the observed, and this may perhaps be explained in the manner suggested by Ramage. I have therefore divided each series into two groups, the first ending and the second beginning with the lowest member of the series which contains a CH_2 group linked to two carbon atoms. Thus, of the alkyl chlorides, the first group contains CH_3Cl , $\text{CH}_3\text{CH}_2\text{Cl}$, and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$, and the second group begins with propyl chloride, so that all its members contain one or more $\text{C}-\text{CH}_2-\text{C}$ groups.

In the case of the ethers, esters, and other compounds which contain two alkyl radicals, a series is regarded as homologous when one radical remains unaltered and the other increases by stages of CH_2 . The variable radical only is considered in dividing the series into the two groups; thus, although propionic acid contains a $\text{C}-\text{CH}_2-\text{C}$ group, it remains unchanged in the propionic esters, the first group of which consists of methyl, ethyl, and propyl propionate, the second beginning with the last-named ester. (See Table II.).

TABLE II.

Group.	Lower members.		Higher members.	
	Number of values of Δ .	Mean difference. Calculated—observed.	Number of values of Δ .	Mean difference. Calculated—observed.
Alkyl chlorides	2	+ 2.70°	5	- 1.04°
Alkyl bromides	2	+ 1.12	5	- 1.25
Alkyl iodides	2	+ 0.52	3	- 1.0
Isoparaffins	—	—	2	+ 0.57
Toluene, &c.	1	0.45	3	+ 0.68
<i>o</i> -Xylene, &c.	1	+ 6.1	1	- 0.5
<i>m</i> -Xylene, &c.	1	+ 4.25?	1	+ 4.0?
<i>p</i> -Xylene, &c.	1	0.15	1	+ 0.65
Diethyl benzene, &c. ..	—	—	1	- 0.5
Olefines, $\text{H}_2\text{C}=\text{CHR}$..	—	—	3	- 2.35?
Olefines, $\text{RHC}=\text{CHR}$..	—	—	3	+ 0.5?
Polyethylene	—	—	2	- 3.85?
Ethers	3	+ 8.2	13	+ 1.12
Aldehydes	2	+ 2.0	4	+ 1.3
Hydrosulphides	2	+ 3.55	1	- 0.5
Amines	2	+ 8.2	4	+ 1.7
Esters	47	+ 4.92	67	+ 1.53

Associating Substances.

Cyanides	1	+ 12.65	4	+ 2.9
Nitromethane, &c.	2	+ 11.1	1	+ 3.85
Ketones	1	+ 6.2	3	+ 2.85
Fatty acids	2	+ 5.87	7	+ 1.58
Fatty alcohols	2	+ 12.87	5	+ 5.24

Of the seventeen series of non-associating substances there are only five for which the mean difference between the calculated and observed values of Δ for the higher members exceeds 1.5° .

1. The *m*-xylene series. Here there is only one value, which, I think, is doubtful.

2. The olefines, $\text{H}_2\text{C}=\text{CHR}$. Here two of the three individual differences are less than 1.5° ; the temperatures are all below 0° , and are somewhat uncertain.

3. The polymethylenes. The difference for pentamethylene and hexamethylene differs by less than 1° from the calculated value. The boiling-point of heptamethylene appears very doubtful.

4. The amines. Differences somewhat erratic; three within 1.5° and two within 0.5° . Octylamine and nonylamine clearly incorrect and not values.

5. The esters. Although Ramsay and Shields include these substances as non-associating, there is, I think, reason to suspect slight association.

It will be seen that the differences are greater for associating than for non-associating substances; also that they are greatest for the alcohols and least for the acids, although the factor of association is very high for both these series. In order to arrive at an explanation of these facts the effect of replacing hydrogen by chlorine may first be considered.

The boiling-point of hydrogen chloride is not yet known accurately, but it must be about -80° . Thus, by replacing an atom of hydrogen in the hydrogen molecule by chlorine, the boiling-point is raised from 20.4° abs. to about 193° abs., or about 173° . On replacing an atom of hydrogen in methane by chlorine, the rise of boiling-point is from 108.3° to 249.3° , or 141° . Ascending the series of paraffins the rise of boiling-point due to the replacement of hydrogen by chlorine diminishes rapidly at first, and then more slowly, being only 58.5° in the case of octane. Thus the influence of the chlorine atom becomes relatively smaller as the formula weight of the alkyl group increases.

Consider, now, the effect of replacing a hydrogen atom by a hydroxyl group. In the formation of water from hydrogen gas the boiling-point is raised no less than 352.6° , from 20.4° abs. to 373° abs., or in the ratio of 1:18.3; in the case of methane the rise is 221.8° , from 108.3° to 377.7° , or in the ratio of 1:3.12; with octane the rise is 65.4° , from 398.6° to 464° ; and with hexadecane it is only 56.5° , from 560.5° to 617° , the ratio being 1:1.10.

It will be seen that in the case of hydrogen the influence of the hydroxyl is enormously greater, and in the case of methane very much greater, than that of chlorine in

explanation of the very low values of Δ for the alcohols, and the moderately low values for the acids is thus afforded.

It would take up far too much time and space to give full details of the boiling-points of all the compounds considered, with the observed and calculated values of Δ ; but it may, I think, be stated that the difference between the boiling-point of any non-associating organic compound which contains at least one $\text{C}-\text{CH}_2-\text{C}$ group, and that of its next higher homologue (at any rate up to temperatures of about $300^{\circ}\text{C}.$), may be calculated with an error rarely exceeding 1.5° and generally under 1° , by means of the formula $\Delta = \frac{144.86}{T_{\text{boil}}^{1.48} \sqrt{V}}$. The formula

seems also to be applicable to any ester which contains at least five atoms of carbon in the variable alkyl or acyl group (the mean error for 40 values of Δ is $+0.93^{\circ}$), and with smaller error when the number of carbon atoms is still larger;* it is probably also applicable to the higher fatty acids, cyanides, ketones, and nitro-compounds.

Comparison of Molecular Volumes.

The fundamental idea on which both Kopp and Schröder based their methods of calculating the molecular volumes of organic compounds from the atomic volumes of the component elements was the constancy of the increase in molecular volume for each addition of CH_2 . With regard to this point the question was greatly discussed whether the comparison should be made at the same temperature, say $0^{\circ}\text{C}.$, or at the boiling-points of the compounds under the same pressure. Later, when Van der Waals brought forward his conception of corresponding states, it was thought probable that the comparison should be made at corresponding or equal reduced temperatures; that is to

TABLE III.

Paraffin.	A.		B.		C.		D.		E.	
	Molecular volume.	Δ .	Molecular volume.	Δ .	Molecular volume.	Δ .	Molecular volume.	Δ .	Molecular volume.	Δ .
n-Pentane	111.33	15.44	117.80	22.13	116.13	20.09	116.13	21.06	309.3	56.8
n-Hexane	126.77	15.69	139.93	22.63	136.22	20.18	137.19	21.49	366.1	60.2
n-Heptane	142.46	15.88	162.56	23.70	156.40	20.51	158.68	21.83	426.3	62.6
n-Octane	158.34		186.26		176.94		180.51		488.9	

raising the boiling-point, but that on ascending the series of paraffins to octane the influence of the hydroxyl group diminishes until it is little greater than that of the chlorine atom, and it is quite probable that with hexadecane it would be somewhat less. This is, no doubt, to be explained by the fact that the molecules of water and of the lower alcohols are highly associated in the liquid, but not in the gaseous state, and therefore, in order to vaporise the liquids, this molecular attraction must be overcome, and the temperature must therefore be raised. The molecular association diminishes, however, as the series of alcohols is ascended, and is probably slight in the case of octyl alcohol. If so, it would appear that the effect of the hydroxyl group—apart from association—in raising the boiling-point is not very different from, and is probably somewhat less than, that of the chlorine atom, and that the difference between the boiling-points of the lower alcohols and of the corresponding chlorides is entirely due to molecular association in the liquid state.

With the acids there is association in the gaseous as well as the liquid state, and since, according to the tables given by Ramsay and Shields, the factor of association for a liquid fatty acid at its boiling-point is rarely greater, and in most cases is somewhat smaller, than for the corresponding liquid alcohol, the molecular attraction to be overcome on vaporisation must be considerably less for the acid than for the corresponding alcohol, and the resulting rise of boiling-point above the normal value must be less. An

say, at temperatures which bear the same ratio to the critical temperatures. If the generalisations of Van der Waals were strictly true, the boiling-points under corresponding pressures would be corresponding temperatures, but that is not usually the case. The comparison may therefore be made either at equal reduced temperatures or at the boiling-points under equal reduced pressures; or, lastly, it may be made at the critical points themselves, and, thanks to the law of Cailletet and Mathias, the critical volumes can be ascertained with a great degree of accuracy.

In order to find whether the difference in molecular volume for each addition of CH_2 is really constant, it is best to examine such perfectly normal substances as the paraffins, and the data for four consecutive members of the series—*n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane—are fortunately available.

In Table III. the molecular volumes and the differences, Δ , for an addition of CH_2 are given under the following conditions:—

* Thus the observed boiling-point of *n*-hexyl formate is 173.6° , and the value of Δ calculated from the formula is 22.8 , giving 176.4° as the boiling-point of the next higher homologue. This agrees very well with the observed boiling-point of *n*-heptyl formate, 176.3° , but not with that of *n*-hexyl acetate, 169.2° . Again, the observed boiling-point of methyl caproate (hexoate) is 149.6° , and the calculated value of Δ is 23.0 , giving 172.6° as the boiling-point of the next homologue.

† The observed boiling-point of methyl enanthylate (heptoate) is 172.1° , but that of ethyl caproate is only 166.6° .
‡ The atomic weights ($\text{C}=11.97$, $\text{H}=1$) employed in the original papers are retained.

- A. At 0° C.
- B. At the respective boiling-points under 1 atmosphere pressure.
- C. At equal reduced temperatures (0.6366).
- D. At the respective boiling-points under equal reduced pressures (0.02241).
- E. At the respective critical points.

It will be seen that in every case there is a decided rise in the value of Δ as the series is ascended, but that the rise is relatively smallest when the comparison is made at the particular reduced temperature chosen. At higher reduced temperatures, however, it would be relatively much greater, since it is very marked at the critical point, where the reduced temperature = 1. The rise is also comparatively small at the common temperature 0°, but the comparison would not be satisfactory if a higher common temperature, say 150°, were chosen, because the coefficients of expansion differ considerably; at 150° the values of Δ would be 8.75, 13.45, and 15.38 respectively.

In the case of nine of the lower esters the values of Δ are by no means constant, whether the comparison be made at 0°, at the boiling-point, or at the critical point. The eleven values of Δ vary in the three methods between 16.34 and 18.21, 20.84 and 23.42, 5.43 and 6.17 respectively; but there is not a regular rise with increase of molecular weight.

Both Kopp and Schröder compared the molecular volumes of compounds at their boiling-points under normal pressure, but they deduced quite different values for the atomic volumes of carbon and hydrogen; it is clear, however, that as Δ varies considerably no values whatever for C and H could give accurate results, even in the case of true homologues.

Traube makes the comparison at a common temperature, usually 15°, and takes into consideration both the actual volumes of the molecules and the co-volume, which he assumes to have the same value, $24.5(1+at)$, where $a=1/273$, for all substances. He calculates definite values for the atomic volumes of C and H at a given temperature; thus, at 15°, C=9.9 and H=3.1, or CH₂=16.1, so that here again the difference for CH₂ at a given temperature should be constant.

It does not appear to me that the problem has yet been completely solved, although Traube's method of calculation generally gives much better results than those of Kopp and Schröder.

Comparison of Boiling-points at a Series of Equal Pressures.

The results of this comparison are often exceedingly simple if the two substances compared are very closely related, and if there is no molecular association in either case. Taking, for example, chlorobenzene and bromobenzene, it is found that the ratio of the boiling-points (on the absolute scale of temperature) under equal pressures is constant whatever the pressure may be, or—

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} = 1.0590.$$

A similar result is obtained with the other halogen derivatives of benzene with ethyl bromide and ethyl iodide, with ethyl acetate and propyl acetate, and some other pairs of esters; but in some cases of close relationship—for example, with ethyl formate and ethyl acetate—the ratio is not quite constant, and the formula becomes—

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} + c(T_B - T'_B),$$

where c has a very low value (0.0000417 for these two esters). When there is no close relationship, but the molecules are not associated, the value of c is usually larger—for example, 0.000185 for carbon disulphide and ethyl bromide.

Lastly, when there is no close relationship and the molecules of one or both substances are associated, the formula—

$$\frac{T_A}{T_A^*} = \frac{T'_A}{T'_B} + c(T_B - T'_B)$$

may no longer hold, and a third term may be required, thus—

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} + c(T_B - T'_B) + d(T_B - T'_B)^2;$$

or, in any case, the value of c becomes much higher, as with benzene and ethyl alcohol ($c=0.0008030$) or sulphur and carbon disulphide ($c=0.0006845$).

Behaviour of Liquids when Mixed Together.

There are three points to consider when two liquids are brought together?—(1) Their miscibility, whether infinite, partial, or inappreciable; (2) the relative volumes of the mixture and of the components; (3) the heat evolved or absorbed.

Liquids which are classed as non-miscible rarely, if ever, bear any close chemical relationship. Thus water is practically non-miscible with all hydrocarbons, and with their halogen and many other derivatives; again, mercury, so far as I know, is not miscible with any liquid compound, organic or inorganic. It is true that the higher aliphatic alcohols are almost insoluble in water, although there may be said to be some chemical relationship between them, inasmuch as an alcohol may be regarded as an alkyl derivative of water. But the alcohols may also be looked upon as hydroxyl derivatives of the hydrocarbons, and, the higher the formula weight of the alkyl group, the greater is its influence, relatively to that of the hydroxyl, on the properties of the alcohol. Thus, while the lower alcohols show considerable resemblance to water—for example, in their behaviour with dehydrating agents, such as sodium, phosphoric anhydride, or lime, and in their power of uniting with metallic salts to form crystalline alcoholates corresponding to the hydrates—this resemblance diminishes as we ascend the series, and is generally not observable with the higher members.

On the other hand, the higher the molecular weight of the alcohol the closer is its resemblance to the hydrocarbon from which it is derived. This, as already mentioned, is well shown by the diminishing difference between the boiling-points of the alcohol and paraffin as the series is ascended; it may also be noted that methane was long classed as a permanent gas, while methyl alcohol is a liquid; whereas both hexadecane (C₁₆H₃₄) and cetyl alcohol (C₁₆H₃₃OH) are solids, the former melting at 18° and the latter at 50°.

It may, in fact, I think, be stated that the chemical relationship between water and methyl alcohol is fairly close, while that between water and cetyl alcohol is very distant. So, also, two adjacent members of a homologous series, such as methyl and ethyl alcohol, are more closely related than two members of widely different molecular weight, such as methyl and cetyl alcohol.

Adopting this view, it is, I believe, safe to state that liquids which are chemically closely related to each other are invariably miscible in all proportions.

As regards the relative volumes of a mixture and of its components at the same temperature, it is well known that inequality is the rule and equality the exception; and, further, that contraction is more frequently observed than expansion on admixture. So far, however, as experimental evidence is available, it appears that when the liquids are very closely related to each other the change of volume is exceeding small. For example, with ethyl acetate and propionate in equimolecular proportions, +0.015 per cent; toluene and ethyl benzene, -0.034 per cent; *n*-hexane and *n*-octane, -0.053 per cent; methyl and ethyl alcohol, +0.004 per cent; chlorobenzene and bromobenzene, no change.

When the relationship is less close the changes are usually, but not invariably, larger, and are in some cases positive, in others negative; and it is rarely possible, in the present state of our knowledge, to predict from the nature of the substances—unless one is basic and the other acidic in character—whether contraction or expansion is to be expected. Thus, when methyl alcohol is mixed with

water considerable contraction occurs, although the relationship is less close than between methyl and ethyl alcohol, which expand to a minute extent on mixing.

All we can say with regard to the alcohols is that, the higher the molecular weight—or, if isomeric alcohols are included, the higher the boiling-point—the smaller, as a rule, is the contraction on mixing with water.

Very similar remarks apply to the heat changes which occur on mixing liquids. It appears that in the case of very closely related substances these changes are exceedingly small, or negligible, as is indicated by the very minute change of temperature which has been observed, thus:—Ethyl acetate and propionate, -0.02 ; toluene and ethyl benzene, $+0.05$; *n*-hexane and *n*-octane, $+0.06$; methyl and ethyl alcohol, -0.10 ; chlorobenzene and bromobenzene, 0.00 .

It might be expected that in the case of less closely related substances contraction would be accompanied by evolution of heat and expansion by absorption of heat, but this is by no means invariably the case; for example, on mixing 40 gm.-molecules of propyl alcohol with 60 gm.-molecules of water there is a contraction of 1.42 per cent, but a fall of 1.15° in temperature was observed. Taking the alcohols as a group, it is found that, the higher the boiling-point, the smaller is the heat evolution, or the greater the absorption on admixture with water.

Properties of Mixtures.

The behaviour of two non-miscible liquids when heated together is well known, and I need only refer to the fact that the vapour pressure is equal to the sum of the vapour pressures of the pure components at the same temperature; that the boiling-point is the temperature at which the sum of the vapour pressures of the components is equal to the pressure under which the liquid is being distilled, provided that evaporation is taking place freely, and the vapour is not mixed with air; and, lastly, that the composition of the vapour is independent of that of the liquid (so long as both components are present in sufficient quantity), and is expressed by the equation—

$$\frac{x_A}{x_B} = \frac{P_A D_A}{P_B D_B}$$

where x_A and x_B are the relative weights of the two components in the vapour, P_A and P_B their vapour pressures at the observed boiling-point, and D_A and D_B their vapour densities.

The vapour pressure, boiling-point, and vapour composition, then, can be calculated for non-miscible liquids, and it has been stated that such liquids have never any close chemical relationship, and are usually not related at all.

On the other hand, it has been mentioned that when the chemical relationship is very close the liquids are invariably miscible in all proportions, and that there is very little, if any, volume or heat change on admixture.

So, also, the vapour pressure and boiling-point of a mixture of closely related liquids are easily ascertained from those of the pure components, and the composition of the vapour bears a simple relation to that of the liquid.

The vapour pressure of the mixture is given, at any rate with a very close approach to accuracy, by the equation $P = mP_A + (100 - m)P_B$, where P , P_A , and P_B are the

vapour pressures of the mixture and of the components, A and B , at the observed boiling-point, and m is the molecular percentage of A .

Van der Waals concluded from theoretical considerations that this relation should be true when the critical pressures are equal and the molecular attractions agree with the formula proposed by Galtzine and by D. Berthelot, $a_{12} = \sqrt{a_1 a_2}$, where a_{12} represents the attraction of the unlike molecules, and a_1 and a_2 the respective attractions of the like molecules. That is certainly the case with

chlorobenzene and bromobenzene, which, as already mentioned, show no heat or volume change on admixture, for the maximum difference between the observed and calculated pressure in three experiments was less than 0.1 per cent.

But the relation is, at any rate, very nearly true for closely related substances when the critical pressures are not equal, for in the case of methyl and ethyl alcohol the difference between the observed and calculated pressure was within the limits of experimental error, and with four other pairs of closely related substances the greatest mean difference (for three readings each) was only 0.6 per cent. It is not, however, as Speyers suggested, true for all non-associated substances, whether closely related or not; indeed, chemical relationship seems to be much more important than the state of molecular aggregation, for the relation is true for methyl and ethyl alcohol, while it is altogether untrue for benzene and hexane.

The boiling-point of a mixture of closely related liquids may be ascertained from the vapour pressures of the components, but not so simply as in the case of non-miscible liquids, because the boiling-point depends on the composition of the liquid.

In order to calculate the boiling-points of all mixtures of two closely related liquids under normal pressure, we should require to know the vapour pressure of each substance at temperatures between their respective boiling-points under that pressure. Thus, chloroform boils at 132.0° and bromobenzene at 156.1° , and we must be able to ascertain the vapour pressure of each substance between 132° and 156° .

The percentage molecular composition of mixtures which exert a vapour pressure of 760 m.m. must then be calculated at a series of temperatures—say, every two degrees—between these limits by means of the formula—

$$m = 100 \cdot \frac{P_B - P}{P_B - P_A}$$

where, in this case, $P = 760$.

Lastly, the molecular percentages of A , so calculated, must be mapped against the temperatures, and the curve drawn through the points will give us the required relation between boiling-point and molecular composition under normal pressure. In the case of six pairs of closely related liquids the greatest difference between the observed temperature and that read from the curve constructed as described was 0.27° .

For liquids which are not closely related, the differences are usually much greater, and particular mixtures of constant (minimum or maximum) boiling-point are not unfrequently met with, especially when the molecules of one or both substances are associated in the liquid state.

The formula for the composition of the vapour from a mixed liquid suggested independently by Berthelot and by Wanklyn,—

$$\frac{x_A}{x_B} = \frac{W_A P_A D_A}{W_B P_B D_B}$$

(where x_A and x_B , P_A and P_B , D_A and D_B have the same meaning as in the equation for non-miscible liquids, and W_A and W_B are the relative weights of the two components in the liquid mixture), was shown by F. D. Brown to be incorrect, and he proposed the simpler formula—

$$\frac{x_A}{x_B} = c \frac{W_A}{W_B}$$

where c is a constant which does not differ greatly from $\frac{P_A}{P_B}$. The subject was investigated mathematically by

Duhem and by Margules, and experimentally and mathematically by Lefheldt and by Zawidski. The two last-named observers deduced workable formulae from the fundamental equation of Duhem and Margules, and it is noticeable that both Lefheldt's and Zawidski's formulae, in their simplest

form, become identical with Brown's. Zawidski's, however, assumes the form—

$$\frac{x_A}{x_B} = \frac{P_A}{P_B} \cdot \frac{W_A}{W_B}.$$

This formula is certainly not, as a rule, true for mixtures of liquids which are not closely related; but, on the other hand, in the very few cases examined the equation

$\frac{x_A}{x_B} = c \cdot \frac{W_A}{W_B}$ appears to hold for those mixtures for which the equation—

$$P = \frac{m P_A + (100 - m) P_B}{100}$$

is true; that is to say, generally, for closely related liquids.

The question, however, whether $c = \frac{P_A}{P_B}$ is an open

one; but it is interesting to remark that if this equality holds it should be possible in many cases to calculate the vapour pressure at any temperature, the boiling-point under any pressure, and the composition of the vapour of any mixture of two closely related liquids, if the boiling-point of one of them under any one pressure, and the vapour pressures of the other within sufficiently wide limits of temperature, are known. For the boiling-points on the absolute scale of the two liquids at the same pressure bear a

constant ratio to each other, or $\frac{T_A}{T_B} = \frac{T'_A}{T'_B}$; hence the

vapour pressures or boiling-points of one substance can be calculated if those of the other are known. Again, from the vapour pressures of the pure substances we can calculate the vapour pressures and the boiling-points of all

mixtures; and, lastly, if $c = \frac{P_A}{P_B}$, we can make use of Brown's formula,—

$$\frac{x_A}{x_B} = c \cdot \frac{W_A}{W_B},$$

to calculate the composition of the vapour from all mixtures without carrying out special experiments to find the value of c . It is, therefore, a matter of considerable

interest to ascertain whether c is really equal to $\frac{P_A}{P_B}$ or not.

When the equation $P = \frac{m P_A + (100 - m) P_B}{100}$ does not

hold good, a modification of Brown's formula, or that of Leheldt, or of Zawidski, must be employed to calculate the vapour composition, and the constants for those formulæ must first be determined experimentally.

Other physical properties, such as the refractive power of mixtures, might be considered, but I will only refer to the critical temperature and pressure. In 1882, Pawlewski stated that the critical temperature of a mixture could be calculated from those of the components by the formula

$$\theta = \frac{m \theta_A + (100 - m) \theta_B}{100}, \text{ where } m \text{ is the percentage by}$$

weight of A; and G. C. Schmidt, in 1891, carried out experiments to test the correctness of the statement, purposely choosing substances of widely different physical properties. The differences between the calculated and observed temperatures were not, as a rule, very great, rarely exceeding 4°, and Schmidt considered that they might, to some extent, be accounted for by partial decomposition of one or other component.

Such determinations are, however, liable to serious errors. It is exceedingly difficult to fill a tube with the required amount of a liquid mixture of known composition quite free from air, and although the composition of the very small amount of liquid employed might be determined after the experiment from its specific refractive power, it

would be necessary to know the specific refractive powers of the two components and of mixtures of them. Schmidt does not state how he prepared his mixtures and determined their composition.

Again, when a liquid mixture is heated in a sealed tube, fractionation goes on, so that the more volatile component tends to accumulate in the upper part of the tube, leaving the less volatile component in excess below, and unless a stirring arrangement, such as that devised by Kuenen, is employed, many hours would elapse before complete admixture by diffusion took place at the critical point.

By far the most important and accurate experiments on this subject have been carried out by past or present pupils of Professor Kamerlingh Onnes, notably by Professor Kuenen; and it is quite certain that the formula of Pawlewski cannot be generally true for mixed liquids, for, just as we may have mixtures of minimum or maximum boiling-point, so also, as Kuenen has shown, mixtures of minimum or maximum critical temperature may exist. Thus the critical temperature of carbon dioxide is 31.1°, and of ethane 32.0°, but that of a mixture containing 30 molecules per cent of carbon dioxide is 18.8°. The question remains, however, whether some such law as that proposed by Pawlewski may not hold good for closely related substances. In certain cases, when the relationship is very close (for example, C₆H₅Cl and C₆H₅Br), the critical pressures are equal, or very nearly so, and it seems probable that the critical pressure would be the same for any mixture as for the components. Such a case as this would be likely to give the simplest possible relation between the critical temperatures of a mixture and those of its components; and although the critical temperatures of these substances are inconveniently high, there are, no doubt, others which might be employed—perhaps ethyl chloride and bromide, or possibly carbon dioxide and carbon disulphide. I imagine, however, that Pawlewski's formula would be more likely to hold if m represented the molecular percentage, and not the percentage by weight of A.

In the case of homologous compounds, paraffins, ethers, esters, and so on, the critical pressures are not equal, and it would be necessary to find whether the critical pressures of mixtures are represented by the formula

$$P = \frac{m P_A + (100 - m) P_B}{100} \text{ (where } m \text{ is the molecular per-}$$

centage of A), and also whether any such simple formula is applicable to the critical temperatures.

Kuenen has made some observations with mixtures of ethane and butane containing 2.5 and 5 molecules per cent of butane, and at the conclusion of his paper he says:—"If there was a simple law connecting the critical constants of mixtures with those of the constituents, we might calculate the constants for the second substance (those of the first being known). But such is not the case. Pawlewski's law that the critical temperature is proportional to the composition, expressed in weight units, is very inaccurate, the deviations being sometimes considerable in both directions."

It would, I think, be of great interest if Professor Kuenen could find time to carry out further experiments with mixtures of ethane and butane in order to settle this point, or, perhaps, with *n*-hexane and *n*-octane, both of which can be more easily obtained in a pure state.

From what has been said it may be concluded that, in order to ascertain the normal behaviour of pure substances under different conditions, or to find the simplest relations between the boiling-points, molecular volumes, or other physical constants of a series of substances, or, again, to ascertain the normal behaviour of substances when mixed together, and the properties of the mixtures as compared with those of the components, it is undoubtedly advisable—at first, at any rate—to confine our attention to substances of which the molecules show no signs of association in either the gaseous or liquid state.

In the case of mixtures it is also best to begin with substances which are chemically closely related to each other.

ON THE PROBABLE PRESENCE IN THE SUN
OF THE NEWLY DISCOVERED GASES OF THE
EARTH'S ATMOSPHERE.

By G. D. LIVEING, M.A.,
Professor of Chemistry, University of Cambridge.

Soon after the publication of the list of wave-lengths of the rays which Professor Dewar and I found to be emitted by the most volatile gases of the atmosphere, Stassano pointed out that the bright rays of solar protuberances, of which the wave-lengths had been measured by Deslandres and Hale, agreed closely with rays in our list. The wave-lengths need to be determined with very great exactness in order to prove coincidence, and neither set of wave-lengths have, as yet, been measured with such nicety as that. Nevertheless the agreement is sufficient to make it probable that the same gases are concerned in the production of the rays in question.

When, in the *Astrophysical Journal* for June last, Humphreys published a list of wave-lengths of 339 bright rays of the chromosphere and corona, which he had photographed in Sumatra during the total eclipse of May, 1901, I compared this list with our list of the wave-lengths of rays of the most volatile atmospheric gases, and with those of xenon and krypton, which we had subsequently published, and with those of argon. The result was that of the 339 rays in Humphreys' list 209 do not differ in wave-length by more than one unit from rays emitted by gases of the earth's atmosphere. In our published lists the wave-lengths are given to four figures only in Rowland units; those of Humphreys' list are given to tenths of a unit, so that we are far from being able to prove coincidence in any case. Nevertheless it is so very probable that every gas which is in the earth's atmosphere is also in the sun's, and so much more likely that rays appearing in the chromosphere at a height of nine seconds of arc, or 4000 miles, above the photosphere, should be due to gases of great volatility than to such metals as titanium or strontium, that it is much safer to treat the question as an open one than to assume that titanium and other metals of high atomic weight are always present in the state of vapour at such a distance from the sun's surface, while much more volatile metals, such as sodium, are not regularly present at a quarter of that height.

We have been expecting from Mr. Baly for a long time past a list of wave-lengths of the gases neon, krypton, and xenon determined with great exactness by the use of a grating. The announcement that these measurements were in progress was made more than two years ago, and when the list appears we shall be in a better position to judge of the nearness of the coincidences. Meantime I have re-measured some of the rays of the most volatile gases, still, however, with only a prismatic spectroscope, so as to get, approximately, the fifth figure of the wave-length, and the result has been in many cases to bring my figures into closer agreement with those of Humphreys. The exactness of Humphreys' wave-lengths is quite as important a factor in the settlement of the question as that of mine. He obtained six photographs on celluloid films with a large concave grating of 30 feet focal length, used without any slit. The first had an exposure of two seconds immediately after second contact. Two seconds sufficed for a change of film, and then the second film was exposed for five seconds, and the third for fifteen seconds; the fourth had a lengthened exposure of two minutes during the middle of totality, the fifth fifteen seconds, and the sixth eight seconds, ending three seconds before third contact. The dispersion of the spectrum was so great that 1 m.m. on the film corresponded to 3.66 Angstrom units, and the range of the spectrum depicted extended from λ 3118 to λ 5204. The latter limit was probably determined by the want of sensitiveness of the films to lower green rays, for it would have been of great interest if the range had included the most characteristic rays of coronium, krypton, and neon. At the upper end the Fraunhofer

line S is just excluded. This, too, is to be regretted, as S is a triple line of iron very unlikely to be reproduced by any mixture of elements excluding iron. The dispersion is ample for very exact determinations of wave-length if there were no difficulties in the way of exact measurement. Humphreys has met these difficulties as best he could, and I do not propose to discuss them now, but I may perhaps explain one or two of them. The station where the photographs were taken was near the northern limit of totality, so that the duration of totality was less than half what it was in the centre of the shadow. From these durations of totality I have calculated that the points of contact of the limbs of sun and moon were each nearly 63° from the diameter of the sun parallel to the line of the moon's apparent motion; and the instrument was so arranged that the ruling of the grating was parallel to that line, and in consequence the dispersion at right angles to that line, and the definition affected as little as possible by the moon's motion relative to the sun. During the exposures the tangents at the centres of the small arcs photographed would at first be inclined at about 27° to the direction of the moon's path, and would gradually swing round until at mid totality they would be parallel to it, and then on until they were again inclined at about 27° to that direction, but on the opposite side. This motion tends to blur the definition of the arcs, but the effect would be very small on the first, second, and sixth films, and not great on the third and fifth, but it would be very great on the fourth film for rays emitted only from parts of the chromosphere at much less distance than seven seconds of arc from the sun's limb. Rays emitted from the chromosphere at heights exceeding $7.3''$ would give arcs crossing the direction of dispersion at right angles, and would have well-defined edges on the inside, unaffected by the moon's motion. There are, however, very few of such rays besides H and K and the strong hydrogen and helium rays.

The wave-lengths had to be determined by measuring the distances between the arcs on the films in the direction of dispersion, and interpolating between such of the arcs as could be identified as due to rays of which the wave-lengths were well known. Rays answering to this test would be those above mentioned, namely, H and K and the strong rays of hydrogen and helium, and one or two very characteristic groups, such as the *b* group of magnesium, and, perhaps, the iron triplet 4046-4071. Indeed, on looking through the list I do not see any ray other than these which I could identify with certainty without assuming it to be a reversal of a Fraunhofer line. Humphreys does not say which rays he used as fiducial rays between which he could interpolate. Those which I have just named seem to me too few, and too unequally distributed through the spectrum, to give very trustworthy wave-lengths in all parts of the spectrum. No scale of reference, made with artificial light and the same grating used without a slit, could well be made, or had, in fact, been attempted.

In his list Humphreys gives, against each chromospheric ray, the Fraunhofer line in Rowland's list which has the wave-length nearest to that found for the chromospheric ray. As there are 13,595 lines in Rowland's list in the range of the spectrum embraced by Humphreys' 339 lines, it is not surprising that a Fraunhofer line is to be found for every one of Humphreys' lines, so close that the difference of wave-length is in most cases less than a tenth of a unit and rarely exceeds two-tenths. In discussing his results he evidently assumes the rays to be identical, and ascribes them to the metal (if any) indicated by Rowland. There are, however, some remarkable exceptions to this. They are the rays of helium, and the ultra violet rays of hydrogen which do not appear as Fraunhofer lines. He does not hesitate to ascribe four rays to helium and twenty-four others to hydrogen in preference to identifying them with the nearest Fraunhofer lines. And I think he is right in so doing, notwithstanding the fact that several of these rays have never been observed to be emitted by hydrogen, have not been seen in the spectrum of any star, and are believed to be due to hydrogen only because the wave-lengths found

for them agree closely with the values found by calculation for the prolongation of the well-known series of hydrogen rays.

It is a noteworthy fact, that whereas it is very difficult to get from a tube containing a residue of carefully purified hydrogen any rays of this series above $H\epsilon$, λ 3889, yet when the tubes contain sensible quantities of helium and neon they readily give many lines of the series. Up to $H\epsilon$, λ 3691.5, these rays give very long arcs on Humphreys' films, and are therefore emitted from the upper layer of the chromosphere. Why the presence of helium and neon along with hydrogen should conduce to the development of this series I cannot guess, but whatever the cause it seems to prevail in the sun. Besides the four helium rays above mentioned, other three helium rays might well be identified with arcs on Humphreys' films; λ 3613.78 is much nearer in wave-length to Humphreys' ray λ 3613.8 than the scandium ray with which he identifies it; and λ 4143.92 is nearer to λ 4144.0 than the iron ray to which it is ascribed; and Humphreys' ray 3820.7 gives a very long arc on film IV., and is probably the rather strong helium ray λ 3819.75. There are two rays, λ 3388 and λ 3456.5, giving arcs very long, broad, and hazy, which Humphreys cannot distinguish by measurement from Fraunhofer lines ascribed to titanium, but doubts whether they are really due to that metal. We have found that the most volatile atmospheric gases, probably neon, give rays at about λ 3388.8 and λ 3456.8; the former is rather a strong ray, the latter a weak one. It is possible the solar rays may be identical with them.

That the same gases must be in the atmospheres of the sun and planets appears to me certain. The subject has been discussed by many, but some of them seem to have gone off the track in ascribing the diffusion of these atmospheres to those molecules which, on the kinetic theory, chance to acquire such a velocity as will carry them beyond the attraction of the planet with which they had been associated. Dr. Bryan has calculated that if we suppose the earth's atmosphere to have a definite surface, there is practically no probability that any appreciable amount, of even so volatile a gas as hydrogen can escape with such velocity from that surface that it will not return, provided it be actuated only by the kinetic energy of the gas and by gravitation. Dr. Bryan is careful to point out that other considerations may entirely alter the problem. Now, the postulate of a definite surface to the earth's atmosphere and no gas to be encountered outside it cannot be conceded, nor can the motion of the earth in its orbit be left out of account. If we talk of a gas leaving the atmosphere we need define the limit of the atmosphere, and that is not easy. I do not think that it has any definite limit, but we may make an arbitrary one. Shall we say that when the density is reduced to $1/10^{12}$ of what it is at the earth's surface we have reached that limit? At all events, I do not think there is any evidence that the density of the residuum of gas in planetary space is less than that. If we take Dr. Bryan's figure (derived, I think, from Lord Kelvin), that the number of molecules in 1 c.c. of gas at normal pressure and temperature is approximately 10^{21} , and suppose it reduced to $1/10^{12}$ of that, we shall still have 10^9 molecules left in each cubic centimetre, and a molecule running into such a crowd has as good a chance of being knocked further away as it has of getting back. In fact, if we consider a layer of air at this density, 1 c.c. thick, all round the earth, and remember that the free path is very long, even if we suppose that the molecules all have only the average kinetic energy due to their temperature, many of them will, in a small fraction of a second, have passed far into the layers outside, and it is an equal chance whether the same molecules get back, or others are knocked back instead of them. We do not know at all what the temperature of the residuum of gas in planetary space may be, but it is probably very different from that which a black body would assume if left there. The diffusion of each layer into those above and below it will go on, even at a low temperature, with rapidity; and though

it is true that the layer will contain but an infinitesimal fraction of the earth's atmosphere, yet as it is diffused into neighbouring layers in a small fraction of a second, and there are more than thirty millions of seconds in a year, and the solar system has been many millions of years in settling into its present state, there has been time enough for some considerable interchange of the atmospheres of the sun and earth. It is, however, far more probable that the solar system has settled into its present state from a nearly uniform gaseous mass, than that the materials out of which the sun and planets have been aggregated should have been distributed in such a heterogeneous way as to give a marked distinction between the atmospheres. Nor can we suppose that the sun and planets can have licked up all the gases out of planetary space. For if we could suppose that, and the earth with its atmosphere moving through empty space, the incoherent atmosphere must, I suppose, distribute itself in a long trail throughout the earth's orbit, and this trail would rapidly diffuse into the void space, and the process of diffusion would go on until the amount lost by the earth in its course was counterbalanced by the amount licked up, in fact until gas at a certain average density was distributed throughout the whole of the space in which the earth circulates. That average density will be the same whether we suppose the earth to start with its atmosphere in void space, or to start with a less dense atmosphere in space filled with gas of greater density than that average. Also the distribution of the several gases which have molecules of different masses will ultimately be the same in these two cases. The proportion of gases of smaller molecular mass will increase outwards from the earth's surface as well as from that of the sun, and the interchange between the sun and earth will go on most quickly in the case of the gases of least molecular mass, or, in fact, those which are most volatile. —*Proceedings of the Cambridge Philosophical Society*, vol. xii., Part 2.

ON THE ACTION OF WOOD ON A PHOTOGRAPHIC PLATE IN THE DARK.*

By WILLIAM J. RUSSELL, Ph.D., F.R.S.

It has been shown in former papers that many substances are capable of acting on a photographic plate in the dark,



FIG. 1.

and producing a picture of themselves. Further investigation shows that this property belongs probably to all

* Abstract of a Paper read before the Royal Society, June 16, 1904.

woods, some, however, being much more active than others.

To obtain a picture the wood has to be in contact or at a little distance above the photographic plate, and has to remain there for times varying from half-an-hour to eighteen hours, and to be at a temperature not higher than 55° C.

seen in the wood are very sharp and strongly pronounced in the picture. If the action exerted on the plate be owing to the presence of hydrogen peroxide, as has been previously suggested, no doubt it is produced by the resinous bodies present in the wood, but it is remarkable that there is no action from the dark autumn wood. Experiments

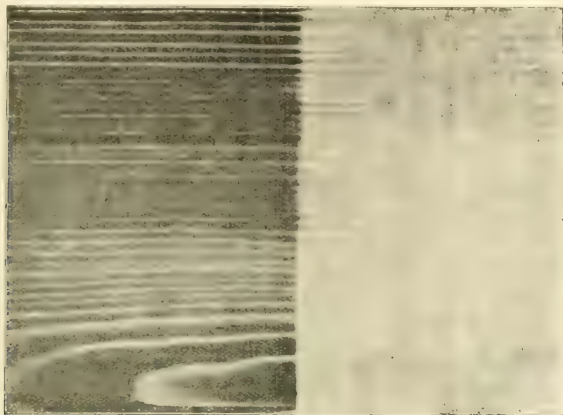


FIG. 2.

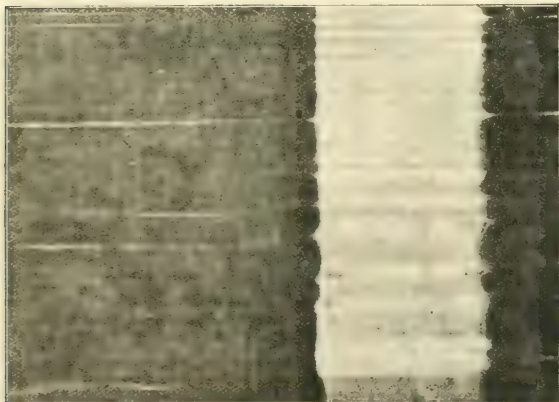


FIG. 3.

The wood of the conifers is very active, and gives pictures which are very definite. Fig. 1 is a picture of a section of a branch of a Scotch fir, and shows well the rings of spring and autumn growth. It is remarkable that the former are very active, producing in this picture the dark rings, and so with the other pictures, the part which is active in the original is dark in the picture. The rings

described in the full paper shows that resin exists in the dark rings, but apparently under such conditions that it cannot escape. Other members of the pine group have been experimented with, and have been found to behave in the same way as the Scotch fir.

With the spruces the action on the plate is not so definite and well marked; the white wood is always active, but in

some cases the dark rings are also active, and the pictures are not so sharp as with the firs. Larch wood gives a very interesting result, for the picture is the reverse of that of the Scotch fir, that is, the dark rings in the wood are the active rings and the light rings are inactive.

With regard to woods other than conifers, oak and beech are both active, and give very good pictures, so also does acacia (*Robinia*), Spanish chesnut, and sycamore; on the other hand, ash, elm, horse chesnut, plane, are comparatively but slightly active. In the full paper lists of woods are arranged according to their activity.

Many foreign woods are very active, but as the annual rings are often not well developed, the pictures they give are of a somewhat different character. The African black wood, rose wood, cocobola, and many others are very active. Several of the foreign woods have a ring of white wood which is quite inactive.

Knots in a wood generally, but not always, give a good picture. Some of the resin in immediate contact with the knot is in some cases but little active. The marked difference in properties of resins from different sources is described, and it is shown how difficult it is to remove it, so that the wood shall be no longer active. Boards that have been exposed to the air for a long time, an oak box a hundred or more years old, rotten wood from the stump of a tree, and even bog wood, have all been found to be still active.

In addition to woods many different resins and allied bodies can, when used alone, be proved to be very active, some naturally much more so than others. Ordinary resins, Burgundy pitch, gum mastic, are very active, asphaltum, dragons blood much less so, but true gums, such as gum senegal and gum arabic, are entirely without action on a photographic plate.

In certain cases the picture obtained on the plate does not resemble the markings which are visible on the wood. With some woods this more commonly occurs than with others. That this picture is persistent in the wood is shown by fresh sections giving the same result. The true bark of a wood is apparently quite without action on a photographic plate, so is the internal pith of a plant.

There is another and a very interesting action, which occurs with wood—it is the great increase of activity which it exerts on a photographic plate after it has been exposed to a strong light. For instance, if a piece of deal be half covered by black paper or tin-foil and be exposed for five to ten minutes to bright sunlight, and then put up in the usual way with a photographic plate, it will give a dark picture where the light has fallen on the wood and only a very faint picture of the part which has been covered. This is shown in Fig. 2. Even comparatively inactive woods, such as elm and ivy, after a short exposure to bright light give good and dark pictures. The action is not an indiscriminate darkening over the whole wood section, but an intensifying of the parts already active. This increase of activity by the action of light appears to occur with all woods. Artificial light, such as that from the electric arc, or from burning magnesium ribbon, act in the same way, so does even a faint light. A piece of wood put at a window for some hours will give a darker picture than a similar piece left in the middle of the room. This increase of power of a wood to produce a picture does not rapidly pass away. After twenty-four hours the action is visibly less, and decreases more rapidly at first than after some days, but it will be a fortnight or may be a month before the wood resumes its former condition. This action, like the former one, is entirely stopped by interposing the thinnest piece of glass or mica between the photographic plate and the active body. An inactive card painted with an alcoholic solution of resin acts in the same way, and turpentine which has been exposed to a bright light acts more strongly on a photographic plate than it does when it has not been so exposed. Again, old printing which is now nearly inactive becomes much more active after exposure to sunlight. Bodies other than those which may contain resin or allied

substances are not affected in this way by light; for instance, flour, sugar, porcelain; metals are not rendered active by sunlight.

The next point was to ascertain which of the constituents of light was most active in producing these effects, and the first experiments were made by simply placing strips of different coloured glass on wood sections, exposing them to sunlight, and afterwards putting them up with the photographic plate in the usual way. Pictures of the results are given in the paper. Red glass entirely prevented any increase in the activity of the wood; in fact, it acted in the same way as a band of black paper or tin-foil would act, and a green glass acted much in the same way, but under a blue glass the activity of the wood was increased to much the same extent as under colourless glass or under no glass. Fig. 3 shows what happens when a red glass and a white glass are placed upon it and is exposed to sunlight. On the right of the figure there was no glass.

Further experiments were made by placing similar pieces of deal in light which had passed through different coloured solutions. Three double-case bell-jars were taken, one was charged with a solution of potassium bichromate, another with copper ammonium sulphate solution, and the third with pure water, and all were exposed to sunlight for four hours. The deal in the red light gave only a faint picture, that in the blue light a dark picture, and that with the pure water was only a slightly darker picture. Resin, guaiacum, copal varnish, white oil paint, and resin sized paper all acted in the same way, and gave similar results.

The light from an arc lamp when passed through a red glass and allowed to fall on a wood section for one and a-half hours produced no effect, but when the same light was passed through a blue glass and fell on a similar wood section for only one hour it produced a dark picture. With liquids this same increase of activity by the action of blue light is produced. Turpentine, which has been exposed to blue light, is more active than when in its ordinary condition.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 30TH, 1904.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, August 10th, 1904.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 211 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 211 samples examined by us during the month, all were clear, bright, and well filtered.

July has been on the whole a dry month, though there has been an excess of rain. The rainfall recorded at

Oxford was 3.35 inches, of which 2.43 inches fell on the 25th, 26th, and 27th. The average fall for July is 2.49 inches; thus we have an excess of 0.86 inch, which, added to the previous excess of 1.37 inches, makes a total excess of 2.23 inches, or 16.7 per cent above the thirty-five years' average.

Our bacteriological examinations of 381 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 377 others from special wells, standpipes, &c., making 758 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	157.2
New River, filtered (mean of 73 samples) ..	8
Thames, unfiltered (mean of 26 samples) ..	7589
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 205 samples) ..	17
Ditto ditto highest	296
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	567
River Lea, from the East London District clear- water wells (mean of 25 samples) ..	11

Of the 303 daily samples taken from the general filter wells of the Metropolitan Water Board, eighteen samples, or 6.0 per cent, were sterile. Seven samples, or 2.3 per cent, contained more than 100 microbes, and of these four samples contained more than 150 microbes per c.c. The seven excess samples contained an average of 177 microbes per c.c. In June nine excess samples contained an average of 152 microbes per c.c.

Our analytical and bacteriological results show that the high degree of purity recorded during the past three months has been surpassed during July. The organic matter in solution in the London waters is lower now than it has been since August, 1901.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

A NATURAL CHEMICAL RULE.

By ARTHUR JAKUES.

THE salts of a considerable number of metals form compounds with ammonia. In some cases it appears that the metal is absorbed into the ammonium radicle, while in others it is more probable that the combination is purely intermolecular—so to express it,—that the salt combines directly in some way with ammonia, without any direct atomic action between the metal and the nitrogen.

A very large number of the metals form compounds in which they function as acid-forming elements, another metal appearing as the base.

A careful examination shows that, in general, no metals form compounds belonging to both these classes. (Of course, in the case of the rarer elements information is not easily obtained).

Whether this is merely coincidence or is due to some common cause it is impossible to say. The marked adherence to the above rule, however, is very noticeable.

The accompanying table shows the behaviour of all the metals with regard to which information has been obtained on the points in question.

In the column marked A are placed those metals which are absorbed into the ammonium radicle; in that marked B, those whose salts combine intermolecularly with ammonia.

Only those metals which appear as acid-forming elements in oxy-salts are placed in the first column; for substances such as "potassium chloroplatinate" are merely double chlorides, and although in certain cases there are grounds

Metal.	Figures as an acid-forming element in oxy-salts	Forms salt which combines with ammonia	
		A.	B.
Aluminium	+	—	—
Antimony	+	—	—
Arsenic (?)	+	—	—
Barium	—	—	+
Bismuth	+	—	—
Cadmium	—	—	+
Cæsium	—	—	—
Calcium	—	—	+
Cerium	—	—	—
Chromium	+	—	—
Cobalt	—	+	+
Copper	—	—	+
Erbium	—	—	—
Gallium	+	—	—
Glucinum	+	—	—
Gold	+	+	—
Indium	—	—	—
Iridium	—	—	—
Iron	+	—	—
Lanthanum	—	—	—
Lead	+	—	—
Lithium	—	—	—
Magnesium	—	—	+
Manganese	+	—	—
Mercury	—	+	—
Molybdenum	+	—	—
Nickel	—	—	+
Niobium	+	—	—
Osmium	+	—	—
Palladium	—	—	—
Platinum	—	+	+
Potassium	—	—	—
Rhodium	—	—	—
Rubidium	—	—	—
Samarium	—	—	—
Scandium	—	—	—
Silver	—	+	—
Sodium	—	—	—
Strontium	—	—	+
Tantalum	+	—	—
Thorium	—	—	—
Tin	+	—	—
Titanium	+	—	—
Tungsten	+	—	—
Uranium	+	—	—
Vanadium	+	—	—
Ytterbium	—	—	—
Yttrium	—	—	—
Zinc	+	—	+
Zirconium	—	—	—

for considering one metal as acidic to the other, it is impossible to say where the true acidity begins.

Again, only those metals whose salts combine with ammonia are placed in the two divisions of the second column; amides, nitrides, &c., do not come under this heading.

It will be seen that, as far as the information obtained shows, only two metals disobey the above rule, viz., zinc and gold. Zinc forms zincates, while zinc chloride combines with ammonia. Zincates decompose when their solutions are boiled, and the compound of zinc chloride with ammonia does not appear to be formed in solution; so that the metal seems to be on the borderland between the two classes, and is able to partake in a low degree of the properties of each.

Gold forms aurates, also "fulminating gold." This is considered by some to be the compound expressed by the formula (NH₄Au)Cl; others hold it to be ammonium aurate. As there appears to be an extremely explosive compound of the above formula, gold must be reckoned an exception to the rule. It may be said, however, that gold follows the law closely enough to render this substance exceedingly unstable.

CITY OF LONDON COLLEGE, WHITE STREET AND ROPEMAKER STREET, MOORFIELDS, E.C.

MICHAELMAS TERM commences OCTOBER 3rd.

CLASSES and LABORATORY WORK in CHEMISTRY, PHYSICS, BIOLOGY, BOTANY, GEOLOGY, and PHYSIOLOGY. Special preparation for the Examinations of the Pharmaceutical Society, The Conjoint Board, Complete Courses for University Matriculation and Inter, and Final B.Sc., meeting during the Evening and on Saturday.

Full particulars gratis on application to—

DAVID SAVAGE, Secretary.

THE DURHAM COLLEGE OF SCIENCE, NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided for Students of both sexes proceeding to the University Degrees in Science, or in Letters, and for the University Diploma in Theory and Practice of Teaching. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 26th. Lectures begin October 4th, 1904.

Prospectuses on application to the SECRETARY.

UNIVERSITY COLLEGE, BRISTOL. CHEMICAL DEPARTMENT.

Professor—MORRIS W. TRAVERS, D.Sc., F.R.S.
Assistant Professor—FRANCIS E. FRANCIS, D.Sc., Ph.D.
Lecturer—OLIVER C. M. DAVIS, B.Sc., A.I.C.
Lecture Assistant—J. H. STURGES.

THE SESSION 1904-5 begins on OCTOBER 4th. Lectures on Inorganic, Organic, and Advanced Chemistry will be delivered during the Session. The Laboratories are fitted with the most recent improvements for the study of Practical Chemistry and Metallurgy in all its branches. In the Evening the Laboratory is opened on Mondays, and Lectures on Inorganic Chemistry, at reduced fees, are delivered. Several Scholarships are tenable at the College.

CALENDAR, containing full information, price 1s. (by post, 1s. 4d.). For Prospectus and further particulars apply to—

JAMES RAFTER, Registrar and Secretary.

THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

DEPARTMENTS OF CHEMISTRY, TECHNICAL CHEMISTRY, and METALLURGY.

Chemistry.. . . .	Prof. G. G. HENDERSON, M.A., D.Sc., F.I.C.
Technical Chemistry .. .	Prof. THOMAS GRAY, D.Sc., Ph.D.
Metallurgy	Prof. H. HUMBLDT SEXTON, F.C.S., F.I.C.

The Courses of Instruction in these Departments are arranged for Students preparing to become Manufacturing or Analytical Chemists, Metallurgists, or Science Teachers. The courses in Chemistry qualify for the Examinations of the Institute of Chemistry and of the Universities of Glasgow, Edinburgh, and London.

SESSION 1904-5 begins on TUESDAY, SEPTEMBER 27th; the ENTRANCE EXAMINATION begins on MONDAY, SEPTEMBER 19th.

CALENDAR (by post 1s. 4d.), containing regulations for the Association of the College, may be obtained from the SECRETARY, 38, Bath Street, Glasgow. PROSPECTUS free.

REDRUTH SCHOOL OF MINES, CORNWALL.

Session 1904-1905 begins September 7th.

A "Mining Certificate" is awarded to Students passing successfully through the School Course.

PRACTICAL MINING CLASSES, under the Instruction of Capt. WILLIAM HAMSLY (late Government Inspector, South Africa) Distinctions in Mine Surveying in Open Examination five years in succession, including five Medals and Prizes, being all the awards of the City and Guilds of London Institute in 1904 in this subject.

SYLLABUS and every information on application to—

THE REGISTRAR.

MICA

Telephone—
No. 2248
Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., &
102 & 103, Minerva, E.C., London

MICA MANUFACTURERS.

Manufacturers of Mica Goods or Electrical and ALL purposes.

Contractors to His Majesty's Government.

RADIUM

(BROM. PUR.)

FROM STOCK

in

1, 2, & 5 m.g.

Tubes.



ON HIRE,

or at

REASONABLE
PRICES.

Pitchblende, from 2/- to 30/- per piece; in Powder, 2/6 per oz.
Kunzeite, selected, 2/- per gramme. Carnotite, 2/- per oz.
Aeschynite, 2/- per oz.
Spartelite (see NATURE, March 31, 1904, page 523), 2/- per piece.
Chlorophane, 2/- per piece. Samarskite, 2/- per oz.
Zinc Sulphide, green and yellow, 2/6 per tube.
Rad. Residue, 2/- per tube. Polonium, 2/- per gram; 11/- 1/2-gram.
Polonium on Bi. rod, 25/- Willemite, 2/- per oz.
Flexible Sandstone, 5/- to 50/- (See NATURE, June 23, 1904, page 185.)
Monazite, 3/- per oz. Monazit Sand, 1/- per oz.
Diamond chips and powder, 10/- per carat (best quality).
Euklas, Hiddenit, Wagnerit, Phosgenit.
Bar. Plat. Cyan., for Screens, 3/- gramme, 60/- oz. Crystals, 4/- gramme. Screens, 9d. per square inch.
Radio-active Screens, 6d. per square inch. Willemite Screens 6d. per square inch. Electrosopes (special), 21/-.
Sphintarsopes (special), 21/-, 10/6 and 7/6.
Selection of Minerals in Boxes, 2/6, 5/6, 10/6 and 21/-.

NEW ZEALAND VEGETABLE CATERPILLAR; from 2 to 3 inches long, with a stem showing fructification growing out of its head. Specimens may be had from 10/6 to 21/-, according to quality and size.

See NATURE, May 12, 1904, page 44.

Goods may be returned if not approved of, when money will be refunded. Professional Men, Universities, Schools, &c., allowed special terms.

ARMBRECHT, NELSON & CO.

71 & 73, Duke St., Grosvenor Square, W.

THE SIR JOHN CASS TECHNICAL INSTITUTE.

JEWRY STREET, ALDGATE, E.C.

Applications are invited for the Post of LECTURER and DEMONSTRATOR of CHEMISTRY. Commencing salary £150. Full details of the duties may be had from the undersigned. Applications, together with not more than three recent testimonials, must be sent in not later than AUGUST 31st.

CHARLES A. KOHN, Principal.

CHEMICAL MANURE WORKS.

Investor of £5000 to £7000 required for large works in good district, to take part in the management.—Write C. M. W., care of Gould's Advertising Agency, 54, New Oxford Street, London, W.C.

ABSOLUTE ALCOHOL,

FREE FROM DUTY,

FOR SCIENTIFIC AND RESEARCH WORK IN LABORATORIES

To be obtained from

HUGO LORENZ,

7-8, Idol Lane, Great Tower St., London, E.C.,

Licensed Trader in Alcohol and Spirits of Wine.

Stock kept in suitable packages ready for immediate use.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC.

As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,

Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, SHOT, &c.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.

FULL STRENGTH GUARANTEED.

OLDEST and MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes,

LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO., 21, Mincing Lane, London, E.C., who hold stock ready for delivery.

THE CHEMICAL NEWS.

VOL. XC., No. 2336.

ON THE ABSORPTION OF GASES BY CHARCOAL AND COKE.

By G. CRAIG, F.I.C.

It is well known that coke occludes gases in quantity dependent upon its nature and the temperature of its formation. A sample of lignite coke occluded so much that some experiments were made to ascertain the nature of the gases occluded.

The lignite coke was non-vesicular, and was employed in pieces about the size of peas. The charge practically filled the bulb of Jena glass in which it was heated and which was provided with a gas tube and stopcock. After heating to redness, the stopcock was closed, and the bulb and contents allowed to become thoroughly cold. Communication was then made with a graduated vessel containing air, and the coke allowed to become saturated at the ordinary temperature.

By running in mercury the unabsorbed gas was expelled, and the occluded gases were expelled by heating, or more slowly by treating with water.

The unabsorbed gas was found to be nearly pure nitrogen, which suggested the likelihood of the occluded gas being highly oxygenated. On expelling it, however, it was found to be nitrogen also.

Thus, 30 grms. of the coke (=20 c.c. volume) absorbed 220 c.c. of air, and:—

	N.	O.	CO ₂
The unabsorbed gas consisted of ..	99.53	0.47	nil
Gas expelled at 100° C. ..	99.70	0.30	"
Gas expelled at 320° C. ..	95.15	3.64	1.21

Another experiment in which 10 grms. (treated in a much larger bulb) = 6.7 c.c. volume absorbed 140 c.c. of air, and:—

	N.	O.	CO ₂
The unabsorbed gas consisted of ..	87.8	12.2	nil
First portion liberated with water consisted of ..	93.86	6.14	"
Second portion liberated with water consisted of ..	96.00	4.00	"
Third portion liberated with water consisted of ..	98.44	1.56	"
Fourth portion liberated with water consisted of ..	100.00	nil	"

The oxygen absorbed had thus entirely disappeared, and as the coke contained no reduced metal to take it up, and there was practically no CO₂ formed, it must have combined with hydrogen in the coke to form water. Indeed, water was always found in the gas tube after each heating up.

An attempt was made to burn out the hydrogen by maintaining the coke at a dull red heat for some days with some access of air, but the coke thereafter gave the same occlusion results.

This extraordinary and easy oxidation at ordinary temperatures suggested that the lignite coke must present, as it were, a surface of hydrogen, and that in a galvanic couple it would act as a positive element to an ordinary battery carbon. This was found to be the case, and it was even positive to copper in a dilute H₂SO₄ solution.

In the highly interesting occlusion results obtained by Prof. Sir James Dewar at low temperatures with cocoanut charcoal (*vide* CHEMICAL NEWS, vol. xc., p. 73), the same oxidation of hydrogen must take place to some extent unless the sample contains no hydrogen at all. A suitable temperature would be temporarily attained while the gas

was rushing into the bulb and before a poor conductor of insulator like charcoal could prevent it. Such action might explain the observed liberation of more heat than is accounted for by the liquefaction of the gases containing oxygen, and possibly this secondary action might be eliminated by an extremely slow admission and absorption of the gas.

Chemical Laboratory, Glasgow.

SOME METHODS FOR THE DETECTION OF COBALT AND NICKEL.*

By STANLEY R. BENEDICT.

BECAUSE of the great similarity of chemical behaviour between cobalt and nickel, the detection of these two elements in the presence of each other, particularly of small amounts of either, is a problem which presents peculiar difficulties. Many solutions of this problem have been proposed.

For comparison with the methods I wish to propose, I mention what are, so far as I have been able to learn, the most delicate methods yet offered for the detection of cobalt and nickel when both are present in one solution. The one for the detection of cobalt was proposed by Vogel (*Ber.*, 1879, xii., 2314). A saturated solution of ammonium sulphocyanide is added, then a mixture of amyl alcohol and ether added, and the solution shaken. If cobalt be present, the alcohol-ether layer has a blue colour. This method is very sensitive, and will detect 0.5 per cent of cobalt in nickel solutions.

The detection of traces of nickel in an excess of cobalt is a more difficult problem. The most delicate method, up to the present time, is probably the one suggested by Parr (*Journ. Am. Chem. Soc.*, 1897, xix., 341), which depends upon the fact that freshly precipitated nickel hydroxide will liberate iodine from potassium iodide, while cobaltic hydroxide will not. The procedure is as follows:—Bromine water is added to the solution, which is then warmed, next an excess of sodium carbonate added, and the solution brought to boiling. Both the cobalt and nickel are oxidised and precipitated in the trivalent condition by this treatment. The precipitate is well washed upon a filter and hot potassium iodide poured upon it. Free iodine in the filtrate is evidence of the presence of nickel. This test is not as delicate as Vogel's method for cobalt, yet it will detect nickel in many commercial cobalt salts.

My work comprises two methods, one for the detection of nickel only, the other for the detection of both elements. The first of these, viz., for the detection of nickel only, depends upon the fact that if a mixture of nickelous hydroxide and cobaltic hydroxide be treated upon a filter with a cold saturated solution of oxalic acid, the cobalt dissolves to form a complex cobaltoxalate compound, which is only very slowly precipitated by sodium hydroxide, whereas the nickel dissolves as a nickelous compound. The procedure is as follows:—Treat the solution with an excess of sodium peroxide, and warm to boiling. This, as was mentioned by Kassner, oxidises the cobalt but not the nickel (*Arch. Pharm.*, 1894, ccxxii., 226—240). Filter, wash the precipitate until perfectly cold, and pour upon the filter a cold saturated solution of oxalic acid. Pour this through the filter two or three times. To the filtrate add a few drops of a dilute solution of potassium ferricyanide, and then a slight excess of sodium hydroxide. If nickel be present, it is oxidised by the ferricyanide, and a heavy black precipitate of nickelic hydroxide appears, or if only a small amount of nickel be present, the solution darkens considerably. This test is very delicate, detecting as small an amount of nickel as 2 per cent, with comparatively little trouble.

* Read before the Cincinnati Section of the American Chemical Society, February 10, 1901. From the *Journal of the American Chemical Society*, xxvii., No. 6.

Although nickel forms no compound corresponding to the cobaltioxalate compound mentioned above, it has nevertheless been found advisable to use such a reagent as sodium peroxide, which oxidises only cobalt in preference to bromine or chlorine water, which would oxidise both elements, because in the decomposition of the oxalic acid by nickelic hydroxide some of the cobalt salt is reduced to the bivalent condition.

It may be stated that the cobaltioxalate compound formed in this test is of some interest. It has never been formed in this way before, its only method of formation having been by electrolysis, and by leaving a mixture of cobalt hydroxide and potassium tetroxalate made up to a paste with water for a period of from fourteen to twenty-one days (Kehrmann, *Ber.*, 1886, xix., 3101; 1891, xxiv., 2324). It is a green compound, the aqueous solution resembling the solution of a nickel salt in colour. In a manner similar to that outlined above, I have been able to form some new complex salts of other metals, which will be described later.

The second method which I propose is one by means of which either or both elements can be detected, even if one be in great excess, by a single operation in a test-tube. The procedure is extremely simple. It consists in adding an excess of 5N sodium hydroxide (ordinary reagent strength) to the solution, and agitating for half a minute. The results depend upon these facts. If sodium hydroxide be added in excess to a cobalt solution, a dark blue precipitate is at first formed, which is usually regarded as a basic salt. If nickel be entirely absent, this salt changes almost instantaneously to a bright pink compound, viz., the normal cobaltous hydroxide. If, however, nickel is present, this change of colour is retarded, the length of time increasing with the amount of nickel present. As will be seen, this test is extremely rapid, yet its rapidity is fully equalled by its delicacy. If sodium hydroxide be added in excess to each of two cobalt salts, one being an ordinary C. P. salt, and the other a sample of Kahlbaum's "nickel-free" cobalt, a decided difference in the length of time required for the change of colour is evident. In testing for traces of nickel, it is well to have a check tube containing a nickel-free sample for comparison. In this way mere traces of nickel can be detected. In fact, there is every reason to believe that this is the most delicate method so far proposed for the detection of nickel, as well as the most rapid. Its delicacy considerably exceeds that of the potassium iodide test outlined above, as has been determined by making comparative tests. In 10 c.c. of normal cobalt solution containing 1 per cent of nickel solution, the potassium iodide fails absolutely to reveal the presence of nickel, whereas the test outlined above will, in the same strength of solution, detect 0.5 per cent of nickel, and if the amount of cobalt be increased without decreasing the actual amount of nickel, 0.3 per cent of this element can be detected.

The question naturally arises why nickel in such minute quantities retards the change of the blue basic salt to the pink normal hydroxide. This is evidently difficult to answer, and the explanation put forth below is merely offered as a possible one.

This explanation is that when the basic salt, which would have some such formula as $\text{Co}(\text{OH})\text{NO}_3$, loses its NO_3 and begins to take up another OH radical, i.e., becomes, so to speak, nascent, the nickel combines with it to form a nickel cobaltite, which is even more blue than the basic salt. Then, as more of the basic salt changes over, the nickel is finally all taken up, the normal cobaltous hydroxide begins to form, and when a sufficient quantity of this has been formed to hide the blue of the nickel cobaltite, the pink colour makes its appearance. It may also be that the nickel cobaltite is formed immediately upon precipitation, and being unstable, soon breaks up, forming the hydroxides of the two metals.

The reasons for suggesting the formation of nickel cobaltite are as follows:—Firstly, the nickel produces an effect which cannot be accounted for by the physical pro-

perties of its hydroxide; secondly, cobalt is shown to form some cobaltites by the following facts:—(1) The hydroxide is somewhat soluble in a concentrated solution of potassium hydroxide, forming a dark blue solution. I have found that the hydroxide is also considerably soluble (upon warming) in a 5N sodium hydroxide solution in the presence of considerable quantities of salts of some other metals, among which are aluminum, lead, sodium, and lithium. (2) The solutions of these cobaltites are intensely blue, much more so than the original basic salt, a very small amount of cobalt in solution sufficing to give a very intense blue colour. It is therefore possible, if not probable, that the formation of a corresponding nickel compound, which is insoluble and deep blue in colour, may be the cause of the interference with the change of colour of the cobalt precipitate.

As was mentioned, the presence of very small amounts of cobalt can be detected by this method in presence of an excess of nickel. This test depends upon the formation of the blue compound mentioned above, and on the further fact that this colour makes itself evident in a great excess of nickel. For this reason, when sodium hydroxide is added to a solution which contains nickel in excess, if cobalt is present (even somewhat under 1 per cent), this blue colour makes itself visible, especially upon standing a moment, i.e., the hydroxide, instead of being a pure pale green, will have a bluish tinge, more or less deep, depending upon the amount of cobalt present.

In a test of this delicacy it is only natural that certain conditions must be fulfilled lest the results lead to incorrect conclusions. These conditions are as follows:—

1. Other metals besides nickel and cobalt should be absent, since many of these interfere with, or give the reaction outlined above. This is easily accomplished by following the ordinary course of analysis.

2. The solution in which the test is made should be roughly normal (or somewhat stronger) in order that the colour reactions may be best observed.

3. The solution should not contain much free acid (a small amount makes no difference), since the salt formed upon the addition of the hydroxide may interfere somewhat, because, as was mentioned above, the salts of the alkali metals tend to form cobaltites.

The procedure for the detection of the two metals is therefore as follows:—Dissolve the sulphides in concentrated nitric acid, evaporate to dryness, heat gently to expel free acid, and dissolve in a little water. To about 3 c.c. of this solution in a test-tube add 6 to 8 c.c. of sodium hydroxide, cover the mouth of the test-tube with the thumb, mix thoroughly by shaking, and note the result. If cobalt be in excess, the precipitate will have a dark blue colour; if nickel be present in very small amount, the colour will not change immediately, i.e., within four to five seconds, to a bright pink. If, however, the nickel be present in large amount, the change of colour will be retarded for half-an-hour or more, the colour never becoming a bright pink, but changing to a dirty grey. If nickel be absent, the change of colour is practically instantaneous.

If nickel be in excess, the precipitate will not be dark blue, but will have a green colour, which will show more or less bluish tinge, depending upon the amount of cobalt present. If cobalt be absent, the precipitate will be a pale green, and will remain so upon standing.

It will therefore be evident that by this test, which is practically instantaneous and requires no manipulation, it is possible in one operation, carried on in a test-tube, to detect both elements, even if either element be in exceedingly small amount, in a great excess of the other, the test for cobalt being probably as delicate as any hitherto proposed (with the exception of Vogel's test, outlined above, which requires the use of ammonium sulphocyanide, amyl alcohol, and ether), while that for the detection of nickel is considerably more delicate than anything hitherto proposed for this purpose.

For use in ordinary qualitative analysis in college

laboratories where nickel-free cobalt salts are not supplied to students, the test may be modified in one of two ways in order to slightly decrease its delicacy. (1) The students may be told that unless the change of colour is retarded over a minute, nickel may be regarded as absent, or (2) by using, instead of a 5N sodium hydroxide solution, a 10N or 15N solution, when the delicacy is so decreased as to give practically no reaction for nickel in ordinary cobalt salt solutions.

I desire to express my sincere thanks to Dr. J. F. Snell for the valuable advice he has rendered during the progress of this work.

ESTIMATION OF TANNIC AND GALLIC ACIDS.

By W. P. DREAPER, F.I.C., &c.

A RECENT paper on this subject by Messrs. Parker and Payne (*Journ. Soc. Chem. Industry*, 1904, p. 648), recommending the separation of tannic acid as the calcium salt, leads me to think that some further experiments made with the process I brought forward in 1893 may be of value at the present juncture (*Journ. Soc. Chem. Industry*, May, 1893).

In my original process, the tannic and gallic acids were precipitated as lime (or barium) salts, with subsequent titration with copper sulphate solution. The lime method is preferable to the barium one.

The results were expressed in terms of CuO instead of CaO, as in Parker and Payne's process.

In the discussion following one of Dr. Parker's papers at Burlington House, I protested against the leather people setting up a standard for the analysis of tannin materials without reference in any way to the requirements of other trades. Their standard was of such an empirical nature that general chemists could not be expected to accept it.

Even those working in allied industries, such, for instance, as that of dyeing, could hardly be expected to do so.

From this point of view, a process based on the formation of a definite metallic compound is certainly an advance in the right direction, although this idea is, of course, not a new one.

My experiments during the last five years lead me to think that Dr. Parker's statement, that his process agrees in its results with the hide-powder process, is sufficient evidence that it is an unsatisfactory one, and that he is estimating gallic, and perhaps other obscure acids, as tannic acids.

This seems to be the necessary result of using a colloid precipitant. My contention is that such reagents must give way, as the alkaloids have, and that only by a close study of the conditions of precipitation, as metallic salts, can we ever advance in our knowledge of this intricate subject.

For example, the following figures show the percentage of tannic acid (?) in pure gallic acid, as estimated by my improved method and the hide-powder process. The latter is taken as a typical colloid precipitant:—

Dreaper method	0.0 per cent tannic acid.
Dreaper method (but with hide-powder separation)	45.6 " "
Hide-powder process	27.0 " "

As this acid was quite free from tannic acid, these figures are interesting!

The 27.0 per cent error in the case of hide-powder as against the 45.6 per cent error, when copper titration takes the place of the usual weighing of the residue, was at first sight puzzling, but it was found that another serious error (amounting to 18.6 per cent) compensated for that excess in the latter case. This second error was due to the solvent action of the solution on the hide-powder.

What can we say for such a process giving such results as this?

The improved process is put forward, not because it is considered a perfect one, but because it is at least capable of indicating errors of the above order in the hide-powder process. It also indicates a possible way of separating tannic acids into what we regard as their two natural orders, and estimating the gallic acid present at the same time.

By some such comparison as the above we may be able to find out—and possibly eliminate—the errors of known processes.

My modified method requires the following standard solutions:—

1. Standard copper sulphate solution, = 0.05 CuO per c.c.
2. Fifty grms. Am_2CO_3 and 50 grms. sodium sulphite per litre.
3. Twenty grms. lead acetate and 60 c.c. glacial acetic acid per litre.

Fifty c.c. of the original solution, containing from 10 to 15 grms. per litre of tannin material, is titrated with the copper solution after heating with excess of CaCO_3 and cooling. The result, expressed as CuO, represents the total tannic and gallic acids, and from the dyers' point of view the "mordant value" of the extract.

Ferrocyanide indicator is used. A drop of the tannin solution is taken up on a glass rod and pressed on to a doubled sheet of filter-paper. The clear solution on the under sheet is tested with the indicator. One of the best papers to use is brand C. S. and S., No. 589, No. 3. A good paper is necessary.

A second 50 c.c. of tannin solution is taken, and 25 c.c. of No. 2 added. Copper tannate formed on titrating this solution is free from gallate. Towards the end of the reaction the copper salt is precipitated slowly, and two or three minutes must elapse before the final colour reaction is taken. The ferrocyanide solution must be rendered strongly acid with acetic acid.

The process breaks down in the absence of the sulphite, which seems to prevent oxidation. In the case of an unknown extract, the precipitate may be filtered off and weighed at 105°. From this the tannic acid present may be easily calculated, the amount of CuO present being known.

Fifty c.c. are again taken, and 10 c.c. of the lead solution added in the presence of barium sulphate. Shake well, and filter off through dry filter-paper, add a small amount of anhydrous sodium sulphate to the filtrate to remove lead. After five minutes pass through another dry filter-paper. Forty c.c. of this is taken, heated with CaCO_3 , and titrated as in No. 1.

This gives the gallic acid in filtrate, and, by difference, the total tannic acid. This figure will, or will not, agree with No. 2 as the case may be. This will afford a means of estimating the tannic acids (soluble or insoluble) in the ammoniacal solution. This classification is recognised, and this is the only method of separating these two groups quantitatively that the author knows of.

The double filtration to remove the tannate of lead and the excess of sulphate is necessary, as lead sulphate is soluble in calcium acetate solution. The different colours obtained by the ammoniacal titration seem, in some cases, to afford an indication as to their origin. They vary from apple-green to brown through yellowish shades.

It will not do to add the Na_2SO_4 to the solution containing the precipitated tannate. In that case the tannic acid goes into solution. It will be noticed that the difficulty in preventing the decomposition of the lead salt in washing is also obviated.

The following figures working on a pure commercial tannic acid are interesting. (See Table, next column).

The result quoted for gallic acid by the hide-powder process will be noted, because it has been said that one error in this process is due to the absorption of other acids by the hide-powder. These experiments show how useless a blank experiment with distilled water may be.

Acid taken.	Method of separation.	Tannic acid in terms of CuO. Gm.
0.25 grm. tannic acid	.. { Amm. copper	0.083
	.. { Pb method	0.083
0.25 grm. tannic acid + 0.1 grm. gallic acid	.. { Amm. copper	0.084
	.. { Pb method	0.082
0.25 grm. gallic acid	.. { Amm. copper	0.000
	.. { Pb method	0.000

Ammonium carbonate is preferred, although the hydrate will answer. Parker and Payne's experiences with lead nitrate are confirmed by the author. The lead solution recommended above is found to be sufficiently acid to prevent the precipitation of gallic acid. Lead nitrate is more satisfactory for the precipitation of tannic and gallic acids in the presence of sodium acetate.

A single test made on a solution containing equal parts of tannic and gallic acids indicates that about 60 per cent of the gallic acid was carried down with the tannin-collin compound. It is this "carrying down" property of the colloids which is so unsatisfactory. One can never be certain what they will take down with them or subsequently absorb. This seems to be a property common to all the colloids in the insoluble state. The solution after filtering was fairly free from tannic acid. It gave a slight precipitation with the lead acetate solution, but about 98 per cent of the tannic acid present was precipitated. Unfortunately 60 per cent of the gallic acid came down as well. This does not indicate that collin is a satisfactory precipitant.

If collin, in spite of its physical properties, is only a pure gelatin, as Messrs. Parker and Payne assume, it is difficult to see in what way it is superior to the older colloids.

Also, it is probable that the acetic acid added in measured quantity may be under the influence of the precipitated colloids. It is known that some of these bodies have the greatest affinity for such acids. It remains to be seen whether collin acts in the same way.

It is unfortunate, too, that any substance capable of combining with or neutralising $\text{Ca}(\text{HO})_2$ will be returned in the estimation as tannin material. Precipitating as calcium tannate and titration with copper solution gets over this difficulty. Soluble salts would not be estimated.

The direct lime process does not seem to have any advantage over my indirect one. In fact, the opposite seems to be the case when the colloid separation is used. On pure materials, the copper salts agree with the theoretical requirements. The crux of the whole position is the necessity for an efficient precipitating process for the tannic acid.

The lead and copper ammonium separating processes given above are, I believe, far in advance of any colloid method. Whether they are perfect remains to be seen, but they at least open out a new line for work; they separate quantitatively the tannic acids into two classes in a way never before attempted.

It is difficult to see, however, how either calcium or barium hydrate can be used with them. Copper sulphate solution, however, seems to work well.

The colour test put forward as such a feature of the new Parker and Payne process is not new. It is already in everyday use (Proctor, "Leather Industries Lab. Book," p. 88).

It is interesting to note also that Darton's gravimetric estimation works more satisfactorily in the presence of sodium sulphite. With digallic acid the results obtained agree with the theoretical figures. The excess of copper salt present in the solution should be small. The correct amount may be indicated by a preliminary trial as above, and the percentage of copper present in the resulting precipitate estimated at the same time.

The writer considers that the above results may be of interest at the present time. The subject has been approached from quite a different standpoint to that of the leather expert, and different results have been obtained. In the absence of definite and extended

results, collin is regarded with great suspicion as a precipitant by the author. Figures will have to be brought forward to show what its action is on solutions of pure tannic acid containing other acids before any reliance can be placed on it. Does collin differentiate between tannic acid and other organic acids in mixtures of the same? If not, the process stands just where the hide-powder process does to-day, and another series of international conferences will be necessary to deal with this new precipitant.

THE NATURE OF THE PRINCIPAL PHOSPHORUS COMPOUND IN WHEAT BRAN.*

By A. J. PATTEN and E. B. HART.

SUMMARY.

1. PRACTICALLY all of the soluble phosphorus of wheat bran is of an organic nature.

2. The organic compound exists in the bran itself as a magnesium-calcium potassium salt of a phospho-organic acid.

3. The free acid corresponds to the formula $\text{C}_2\text{H}_8\text{P}_2\text{O}_9$, and is probably identical with Posternak's anhydro-oxy-methylene diphosphoric acid.

4. The alkali salts of this acid are freely soluble in water. The calcium and copper salts are slightly soluble, while the barium and strontium salts are but sparingly so.

5. The acid and its salts seem to be of wide distribution in the vegetable kingdom, having already been isolated from the seeds of red fir, peas, beans, pumpkin, red and yellow lupine, also from the potato and other tubers and bulbs.

This investigation forms part of the research on the metabolism of phosphorus and sulphur in the animal body conducted under the direction of Dr. Jordan. The physiological rôle of the acids and its salts in animal metabolism will be made the subject of future researches.

INTRODUCTION.

From the work reported in *Bulletin* No. 238 of this Station, and from other work done preliminary to an investigation of the metabolism of phosphorus in animals, it was found that in many of our ordinary feeding stuffs a varying percentage of the organic phosphorus is directly soluble in water and in dilute hydrochloric acid. Data illustrating this point will be found in the following table:—

TABLE I.—Soluble Phosphorus in Oats, Malt Sprouts, and Wheat Bran.

	Total phosphorus. Per cent.	Solvent.	Soluble phosphorus. Per cent.	Percentage of total phosphorus. Per cent.
Oats	0.355	{ Water	0.180	50.0
		{ Hydrochloric	0.096	27.0
Malt sprouts	0.677	{ Water	0.548	81.0
		{ Hydrochloric	0.477	70.0
Wheat bran	1.22	{ Water	1.056	86.5
		{ Hydrochloric	0.95	77.8

It will be seen that wheat bran carries a much larger percentage of phosphorus than any of the others, and that 86.5 per cent is soluble in water.

It was at first supposed that the soluble phosphorus was in combination as nucleins or salts of nucleic acid, but determinations of the amount of soluble nitrogen showed that only about 33 per cent of the phosphorus could be accounted for in this way.

We were therefore led to the conclusion that by far the greater part of the soluble phosphorus was linked up in some other organic combination, since Hart and Andrews have shown that the amount of soluble inorganic phos-

* *Bulletin* No. 250, New York Agricultural Experiment Station.

phorus is exceedingly small (*Bulletin* No. 238, N. Y. Agr. Expt. Station).

INVESTIGATION OF PHOSPHORUS COMPOUND. Attempt to Isolate.

Two pounds of wheat bran was extracted with 6 litres of 0.2 per cent hydrochloric acid for several hours with frequent stirring. The extract was strained through cheese-cloth, and finally filtered through paper.

The filtrate was treated with a large volume of 95 per cent alcohol, which threw down a voluminous, flocculent precipitate. The precipitate was allowed to settle to the bottom, the supernatant liquid syphoned off, and the precipitate washed with alcohol several times by decantation. It was then dissolved in a small volume of 0.2 per cent hydrochloric acid, filtered from an insoluble residue, re-precipitated by alcohol, and washed as before by decantation.

This process was again repeated, the precipitate finally brought upon a filter, washed with absolute alcohol and ether, and dried at 110° C. The resulting product, which weighed 7.2 grms., was a white amorphous powder readily soluble in water.

Its water solution was acid to litmus, and it was precipitated from such solution by solutions of salts of the heavy metals, by the alkali metals and the alkaline earths, also by alcohol and ether.

Chemical analysis showed it to be an organic phosphorus compound coupled with calcium, magnesium, and potassium.

Of this substance:—

0.5004 gm. gave 0.0082 gm. CaO and 0.1327 gm. $Mg_2P_2O_7$, equivalent to 1.13 per cent Ca and 5.80 per cent Mg.

0.512 gm. substance gave 0.0834 gm. K_2PtCl_6 , equivalent to 2.60 per cent K.

0.2174 gm. substance gave 0.1280 gm. $Mg_2P_2O_7$, equivalent to 16.38 per cent P.

0.2122 gm. substance gave 0.1438 gm. CO_2 and 0.072 gm. H_2O , equal to 18.52 per cent C and 3.83 per cent H.

The substance carried also a small amount of nitrogen (0.37 per cent), but this was considered an impurity, and, calculated as a proteid, would lower the carbon and hydrogen to 17.30 per cent and 3.63 per cent respectively.

Composition of Isolated Phosphorus Compound.

	Per cent.
C	17.30
H	3.63
P	16.38
Ca	1.13
Mg	5.80
K	2.60

Similar Compounds Reported by other Workers.

Palladin, working in Schulze's laboratory, isolated from the seeds of black mustard (*Sinapis nigra*) a highly phosphorised compound in combination with calcium and magnesium ("Beiträge zur Kenntniss pflanzlicher Eiweissstoffe," *Zeit. f. Biologie*, Jahrgang 1894, p. 199).

The seeds freed from fat were extracted with 10 per cent sodium chloride solution, filtered, and the filtrate heated to about 80° C. A precipitate separated carrying with it all of the proteid. The larger part of the precipitate went into solution again on cooling, leaving the coagulated proteid in suspension, which was separated by filtration. The filtrate was again heated, and the resulting coagulum collected on a hot water funnel.

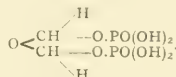
Schulze and Winterstein ("Ueber einen phosphorhaltigen Bestandtheil der Pflanzensamen," *Zeit. f. Physiol. Chem.*, xlii., 90) continued the investigation started by Palladin, and obtained a compound carrying 9.65 per cent C, 2.83 per cent H, and 16.13 per cent P. They thought the substance might be identical with the chief constituent of the globoids found enclosed in the protein kernel of many plant seeds. W. Pfeffer ("Untersuchung ueber die Pro-

teinkoerner und die Bedeutung des Asparagins beim Keimen der Samen," *Jahrbuch für Wissenschaftliche Botanik*, 1872, viii., 147) in conjunction with Brandau found that such globoids consist of a calcium-magnesium salt of an organic body coupled with phosphoric acid. What the nature of this organic combination was they were unable to say.

Winterstein isolated a compound from the seeds of black mustard by extracting with dilute acetic acid ("Ueber einen phosphorhaltigen Pflanzenbestandtheil welcher bei der Spaltung Inosit liefert," *Ber. d. Chem. Ges.*, 1890). The extract was freed from proteid by boiling and filtering when cold. The filtrate was made slightly alkaline with ammonium hydrate and boiled, the resulting precipitate collected on a hot water funnel, and washed with hot water until the wash water reacted neutral. The substance was purified by dissolving in dilute acetic acid, and re-precipitating with ammonium hydrate. On removing the calcium with oxalic acid, a product was obtained carrying 18.44 per cent P and 7.83 per cent Mg. By heating the magnesium salt in a closed tube with concentrated hydrochloric acid for thirty hours, at a temperature of 130–140° he obtained inosite as a cleavage product.

The compound obtained by us from bran by the alcohol method, though still impure, is undoubtedly identical with the one described by these investigators.

Posternak isolated the compound from the seeds of red fir, pumpkin, peas, beans, white and yellow lupine, and also from the potato (*Revue Generale de Botanique*, 1900, xii., 5 and 65; *Comptes Rendus*, cxxvii., Nos. 3, 5, 8). He also isolated and identified the free acid as anhydrous oxymethylene diphosphoric acid with the following formula:



The method adopted by Posternak was the following:—

The material was extracted with dilute hydrochloric acid and filtered, the filtrate was made alkaline with sodium hydrate, and precipitated with calcium chloride. The calcium chloride precipitate was filtered, washed, and finally dissolved in dilute hydrochloric acid. Sodium acetate was added to the solution to replace the free mineral acid by acetic acid, and copper acetate added in excess. The copper precipitate was filtered, thoroughly washed with water, and decomposed by hydrogen sulphide.

The copper sulphide was removed by filtration, and the excess of hydrogen sulphide removed by pumping air through the liquid. It was then evaporated in a vacuum over sulphuric acid.

We found it very difficult to remove the last traces of calcium by this method, and have modified it by substituting barium chloride for calcium chloride. This admits of a very thorough washing at this stage of the operation, as the barium salt is much more insoluble than the calcium salt, and also admits of a complete removal of the barium as a sulphate.

Method of Preparation of Free Acid.

The method finally adopted by us is as follows:—

The bran was extracted with 0.2 per cent hydrochloric acid, strained through cheese-cloth, and filtered through paper. Since the compound is present in bran as a calcium-magnesium potassium salt, it was precipitated directly with copper acetate, by which means we were able to remove the greater part of these bases. After washing the copper precipitate it was suspended in water, and decomposed by hydrogen sulphide. The filtrate from copper sulphide was made alkaline with sodium hydrate, and precipitated with barium chloride. The barium salt was washed until free from alkali, suspended in water, and dilute sulphuric acid added in sufficient quantity to decompose the salt and throw down the barium as a sulphate. After removal of the barium sulphate by filtration the

filtrate was again precipitated in alkaline solution with barium chloride, and treated as before. This process was repeated a third time, and after final removal of the barium, copper acetate was added in excess. The copper precipitate was filtered at the pump, thoroughly washed with water, and finally suspended in water and decomposed by hydrogen sulphide. The copper sulphide was removed by filtration, and the filtrate evaporated on the water-bath to a syrupy consistency.

Analysis of the acid dried at 110° gave the following results:—

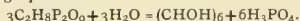
0.7207 grm. substance gave 0.2811 grm. CO_2 and 0.2202 grm. H_2O , equivalent to 10.63 per cent C and 3.38 per cent H.

0.1039 grm. substance gave 0.097 grm. $\text{Mg}_2\text{P}_2\text{O}_7$, equivalent to 25.98 per cent P.

	Found.	Calculated for $\text{C}_2\text{H}_6\text{P}_2\text{O}_8$.
C	10.63	10.60
H	3.38	3.36
P	25.98	26.07

Decomposition of Compound into Inosite and Phosphoric Acid.

Heated with concentrated mineral acids it is broken up quantitatively into inosite and phosphoric acid, after the following equation:—



Posternak obtained 97.8 per cent of the total carbon of the acid decomposed as inosite. In our investigation an unweighed portion of the acid was heated in a closed tube with 50 c.c. of 30 per cent sulphuric acid at a temperature of 155 – 160° for five hours. After cooling, the tube was opened, and the contents washed into a beaker. The sulphuric and phosphoric acids were removed by barium hydrate, and the excess of barium by carbon dioxide. The filtrate was evaporated nearly to dryness, taken up with hot water, and filtered from remaining barium carbonate. The filtrate was then treated with absolute alcohol and ether until a cloudiness was produced, when it was allowed to stand in the cold. A crystalline precipitate soon separated, which was obtained pure after once re-crystallising. It gave the reactions of Scherer and Gallois, and melted at 218 – 219° (uncor.). Inosite melts at 218° (uncor.).

Carbon and hydrogen determinations were made on the substance dried at 110° .

	Found.	Calculated for inosite. $\text{C}_6\text{H}_{12}\text{O}_6$.
C	39.59	40.00
H	6.78	6.66

Properties of Anhydro-oxymethylene Diphosphoric Acid.

The free acid dried slowly over sulphuric acid is a very thick transparent liquid of a yellowish brown colour. It is soluble in all proportions in water and alcohol, insoluble in ether, benzene, chloroform, and glacial acetic acid. It has a very sharp acid taste. Heated to 110° it becomes decidedly brown without decomposition. The alkali salts of the acid are freely soluble in water. Water solutions of the free acid are precipitated by ferric chloride, the precipitate being soluble in an excess of the reagent. Silver nitrate precipitates solutions of the free acid only after a liberal excess of the reagent has been added. The precipitate is insoluble in excess of the reagent. The free acid is not precipitated by the chlorides of magnesium, calcium, barium, or strontium, due to the liberation of free hydrochloric acid. However, when solutions of the alkaline salts of the free acid are treated with the above reagents, a precipitate is formed.

The magnesium and calcium salts are somewhat soluble in water, the barium and strontium salts very sparingly soluble. The magnesium salt is easily soluble in acetic acid, the calcium salt less so, while the barium and strontium salts are very insoluble. All are readily soluble in mineral acids.

The free acid is tetra-basic and forms two salts, the one a normal salt, the other an acid salt. The normal salt reacts neutral to phenolphthalein, while the acid salt reacts neutral to methyl-orange, which may be shown by the following determinations:—Ten c.c. of a solution containing 0.0648 grm. of the acid titrated to phenolphthalein with decinormal barium hydrate required 10.9 c.c. or 0.0748 grm. barium. 0.0648 grm. of the acid should require 0.0749 grm. barium to produce the normal salt ($\text{C}_2\text{H}_4\text{P}_2\text{O}_8\text{Ba}_2$). Ten c.c. of the same solution titrated to methyl-orange with decinormal barium hydrate required 5.1 c.c. or 0.035 grm. barium. 0.0648 grm. of the acid should require 0.0343 grm. barium to produce the acid salt ($\text{C}_2\text{H}_6\text{P}_2\text{O}_8\text{Ba}$).

Quantitative Estimation of the Acid in Wheat Bran.

We extracted 10 grms. of bran to 500 c.c. with 0.2 per cent hydrochloric acid, made 100 c.c. alkaline with sodium hydrate, precipitated with barium chloride, filtered, and washed free from alkali.

The phosphorus was determined directly in this precipitate.

	Per cent.
Total phosphorus	1.35
Phosphorus in barium precipitate	0.92
Per cent of phosphorus in barium precipitate to total phosphorus	68.1

Practically all of the phosphorus soluble in 0.2 per cent hydrochloric acid is in this form, as is shown below:—

	Per cent.
Total soluble phosphorus	0.94
Phosphorus in barium precipitate	0.92
Per cent of phosphorus in barium precipitate to total soluble phosphorus	97.9

A DETERMINATION OF NITRITES IN ABSENCE OF AIR.*

By I. K. PHELPS.

DUNSTAN and Dymond have recommended the use of an evacuated flask for the estimation of nitrites by the action of potassium iodide in acid solution (*Pharm. Journ.*, [3], xix., 741). Under these conditions, the nitrous and hydriodic acids interact to produce nitric oxide (which must be kept from contact with gaseous oxygen) and iodine which is determined by decinormal solution thiosulphate. As objections to the process may be cited, the necessity of getting an absolutely gas-tight rubber-jointed apparatus, and the restriction put upon the size of the flask by the two considerations of withstanding the atmospheric pressure when evacuated, and yet being thin-walled enough to allow of the ready heating of the flask. A practical test of a slight modification of the device already used in the determination of nitric acid for getting an inert atmosphere proves to obviate these difficulties and to leave little to be desired in point of accuracy (*Am. Journ. Sci.*, 1902, xiv., 440).

The apparatus used was the same as in the estimation of nitric acid referred to above. It consisted of a boiling flask of 250 c.m.³ capacity closed with a rubber stopper carrying in its two perforations the inlet and exit tubes. A stoppered funnel of 50 c.m.³ capacity with its tube constricted at its lower end was used as an inlet tube, and a glass tube of 0.8 c.m.³ internal diameter, enlarged just above the stopper to a small bulb (to prevent mechanical loss of the solid contents of the flask during the boiling), and bent twice at right angles, served as an exit tube. The flask was supported in the usual manner at a convenient height to allow of heating with a Bunsen burner placed beneath, and the

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, [4], xvii., No. 99.

exit tube was made of a sufficient length to reach to the surface of some mercury contained in a test-tube to the depth of about 3 centimetres.

The analysis was made as follows:—An amount of standard arsenious acid solution, slightly in excess of that required to take up the iodine to be set free later by the nitrous acid, and 25 c.m.³ of a concentrated solution of sodium carbonate were placed in the flask. The stem of the dropping funnel was completely filled with water, the rubber stopper inserted tightly, and the contents of the flask boiled until all air was expelled—a process requiring an active boiling of five to eight minutes. The flame was then removed, the exit tube plunged deep into the mercury by changing the position of the flask on its wire-gauze—which is particularly easy if the gauze is well depressed at the centre, and the flask placed well up on the higher part in the preceding operation—and sulphuric acid (1—4) sucked in through the funnel tube as the flask cooled, the cooling to the room temperature being hastened by standing the flask in a dish containing ice and water. In all, 7 c.m.³ of sulphuric acid were added, this amount having been found by previous experiment to be nearly but not quite enough to neutralise the sodium carbonate used, and also having been found to yield a little more carbon dioxide than the apparatus can hold at the atmospheric pressure. As soon as the diminished pressure in the apparatus was too weak to suck in the acid, the position of the flask was again changed on the wire-gauze, so that the exit tube was raised out of the mercury into the layer of water which had condensed during the preceding boiling, and which then served to trap the apparatus from the outside air. After the acid had been added and had been washed in carefully, the nitrite solution to be analysed containing 2 grms. of pure potassium iodine was introduced into the flask through the funnel, and this was followed by sulphuric acid (1—4) in sufficient amount (5 c.m.³) to render the contents of the flask acid in reaction. Potassium bicarbonate was then added in concentrated solution to alkaline reaction, or until the free iodine had been taken up, the mixture boiled for about five minutes to expel the nitrogen dioxide, cooled, and titrated to colour with decinormal iodine in the presence of starch paste. In making the various additions of liquid to the flask, care was necessarily taken that no air was introduced with the liquid. Table I. records experiments made in this manner upon a solution of commercial sodium nitrite, standardised by treatment with potassium permanganate and oxalic acid in acid solution according to the procedure of Kinnicutt and Nef (*Am. Chem. Journ.*, 1883, v., 388).

TABLE I.

NaNO ₂ taken.	Oxygen value of As ₂ O ₃ taken.	Oxygen value of As ₂ O ₃ found.	Error on oxygen.	Error on NaNO ₂ .
Grm.	Grm.	Grm.	Grm.	Grm.
1. 0.0058	0.01200	0.00061	0.00025+	0.0011+
2. 0.0093	0.01200	0.00066	0.00021+	0.0010+
3. 0.0116	0.03200	0.00065	0.00017+	0.0007+
4. 0.0116	0.03200	0.00065	0.00017+	0.0007+
5. 0.3832	0.05600	0.01120	0.00043+	0.0018+
6. 0.3832	0.05600	0.01118	0.00045+	0.0019+
7. 0.6716	0.08000	0.00160	0.00076+	0.0033+
8. 0.6716	0.08000	0.00158	0.00078+	0.0034+
9. 0.0196	0.03280	0.01003	0.00062+	0.0027+

The experiment numbered 9 is included to show a fact found early in the investigation, namely, the necessity of boiling out the nitrogen dioxide before titrating the residual arsenious acid. It was made like 3 and 4 above up to that point, when instead of boiling out the nitrogen dioxide, cooling, and titrating, it was treated with a slow stream of air bubbling through for fifteen minutes, and then titrated. Evidently the nitrogen dioxide in oxidising affects the arsenious acid slightly.

When the sulphuric acid is being added to the alkaline solution containing the arsenite, iodide, and nitrite, iodine

is set free locally, but it is at once taken up by the alkaline arsenite, so that finally, when the acid reaction is reached, there is only a small amount of it free, no matter how much nitrite may have been used. This condition reduces to a minimum the possibility of a loss of iodine by volatilisation.

As might be anticipated, the two processes show slightly different results, the process outlined above tending to give results in excess of the theory on account of the action of dissolved oxygen, while that of Kinnicutt and Nef should show a deficiency as compared with theory, since the loss of nitrogen oxides is evidenced by the odour when even a very dilute solution of a nitrite is acidified.

NOTICES OF BOOKS.

Gas Works, their Construction and Arrangement, and the Manufacture and Distribution of Coal-gas. Originally written by SAMUEL HUGHES, C.E. Ninth Edition, Revised, with Notices of Recent Improvements, by HENRY O'CONNOR, Assoc.M.I.C.E. London: Crosby Lockwood and Son. 1904. Pp. 416.

WHILE the general outline of this well-known book has been followed, all out of date references have been eliminated, and the latest methods only described. Reference is made to all recent processes used in gas manufacture, such as "carburetted water-gas," "acetylene gas," "Mond gas," &c., and descriptions of all new apparatus are given.

The book is divided into twenty-five chapters, commencing with a historical sketch of gas making, but we need not dwell on the early chapters, as this work, though in its unrevised form, has been a standard work for many years, and is thoroughly known to all gas makers.

In Chapter XIX. we come to an important question in gas making, viz., the various applications of gas for heating, cooking, and other purposes. Owing to the increasing competition of electric lighting, gas makers have had to look in other directions in order to keep up their turnover. Other methods of producing light, such as "water-gas," are described in Chapter XXI., and in Chapter XXII. the various controlling influences which affect the quality and volume of gas are discussed. Mond gas for power purposes is discussed on page 403 (Chapter XXIV.); and in Chapter XXV. the "sliding scale" first proposed by Mr. George Livesey is described. This method, combined with the bonus system of encouraging the workmen to do their best, has had very good results in London.

The book is well arranged and written, and will certainly hold its place as the book for students of gas engineering and gas makers.

There is a good index.

Gold Assaying; a Practical Handbook. By H. JOSHUA PHILLIPS, F.I.C., F.C.S., &c. With numerous illustrations. London: Crosby Lockwood and Son. 1904. Pp. 138.

Most books on metallurgy devote a chapter or two to gold assaying, but we do not at the moment remember a handbook devoted entirely to this subject; there are, of course, text-books dealing with the whole subject of gold, its prospecting, mining, washing, extraction, &c., but a practical handbook such as the one now before us is decidedly an acquisition. It gives the *modus operandi* for the accurate assay of auriferous ores and bullion, and the chemical tests required in the processes of extraction by amalgamation, cyanidation, and chlorination.

We think it would have been an advantage if the sections into which this book is divided had been numbered chapters, but that is a mere detail. The first section deals with the natural occurrence and forms of gold, and the origin of gold deposits; the physical and chemical properties of gold are next considered, followed

by the very important operation of sampling. Then we come to the assay itself, fusing, cupellation, scorification, parting, &c., and the assay of bullion. With regard to cupellation, we do not find any mention of magnesia cupels; these have been recommended by some practical assayers as preferable to the older ones of bone-ash for some purposes; it would be interesting and important to hear some authoritative opinions as to their respective merits.

The last section is on assays in cyanidation, chlorination, and amalgamation processes, together with a synopsis of each of these processes.

The appendix contains a number of useful tables, among which we may call attention to those giving the relative values and names of the weights, measures, and coins used in the principal countries.

The book is well arranged and written, while the illustrations are good and modern. We recommend this book both to beginners and to those in practice who may need occasionally to refer to it on some point.

There is an adequate index.

Analytical Chemistry. By F. P. TREADWELL, Ph.D.

Translated from the Second German Edition by WILLIAM T. HALL, S.B. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

The translator of this work has had the advantage of receiving help and criticism from many brother chemists, besides suggestions from the author as to the proposed alterations in the third German edition, so that the translation presents a good many advantages over the original. It is specially good as regards methods of separation of the less common elements. Gravimetric methods occupy more than half the volume, which would probably be more convenient for use and reference if all the various methods of determining each element, of which a great number applicable in slightly different circumstances are given, were collected together and not given in different parts of the book under the headings of gravimetric and volumetric analysis. Moreover, even this division is not strictly preserved; for instance, the determination of iron by titration is included under gravimetric methods. One very good feature of the book is the recognition of the value of electrolysis for quantitative work; its comparative simplicity of manipulation and convenience well qualify it for the important place the author accords it among other methods of determination.

Chemisch-technische Untersuchungsmethoden. ("The Chemical Examination of Technical Products") Edited by DR. GEORG LUNGE. Vol. I. Fifth Edition. Berlin: Julius Springer. 1904.

In the fifth edition of this valuable work many important changes have necessarily been made, some sections being written by new authors; as, for example, those on the analysis of water and air, which come from the pens of Dr. L. W. Winkler and Dr. K. B. Lehmann respectively. Every part of the work has also been carefully revised, and many additions have been made. The general part by Dr. Lunge gives directions for taking samples, and useful hints on the performance of all ordinary analytical operations by the most accurate and expeditious methods. In the special part in each case the examination and analysis of the raw substances, by-products, and final products are successively described, with great attention to detail, by writers who are specialists in the particular branches they treat of; thus the editor writes the sections on the mineral acids, soda, and chlorine; Dr. Ferd. Fischer is responsible for the chapters on technical gas analysis, and Dr. H. Freudenberg for cyanogen compounds. The repetition of the various tables, which appear in the text on separate sheets so that they may be readily detached from the book and used in the laboratory by themselves, will no doubt be found a great convenience.

The second and third volumes, on which no fewer than thirty-eight collaborators are engaged, are to appear shortly.

Die Beziehungen Zwischen Äquivalent-volumen und Atomgewicht. ("The Relations between Equivalent Volume and Atomic Weight"). By Dr. W. BORCHERS. Halle-a-S.: Wilhelm Knapp. 1904.

At the beginning of this pamphlet Dr. Borchers informs his readers that during the preparation of the new edition of his "Elektrometallurgie" in endeavouring to find an explanation of some apparent anomalies in the Periodic Table he arrived at certain important results relating to the electro-chemical equivalents of the elements, which results are here published and discussed. Taking the equivalent volumes (numerically equal to the equivalent weights divided by specific gravity) as ordinates, the atomic weights being the abscissae, Dr. Borchers obtained systems of curves which exhibit a surprising regularity, and the careful examination of these curves has enabled him to predict the discovery of a certain number of new elements, and to correct the atomic weights of others; for instance, according to the curve for the alkali metals, two unknown elements of this group exist of atomic weight 178 and 221 respectively, the one being probably a liquid and the other a gas; also the curves appear to show that either the right atomic weight has not been ascribed to ytterbium, or else this substance is not elementary. These are only specimens of the predictions the author makes in a paper which will well repay careful reading.

Die Elektrochemische Industrie Deutschlands. ("The Electro-chemical Industry of Germany"). By P. FERCHLAND, Dr. Phil. Halle-a-S.: Wilhelm Knapp. 1904.

THE difficulties attending the amassing of the materials, even for such a small book as this, are undoubtedly very considerable, chiefly because manufacturers exhibit a not unnatural tendency to conceal the most important details of the processes they find most profitable, and the author of this monograph has for this reason been unable to give as complete an account of his subject as might be desirable, in spite of the fact that he has carefully studied all available sources of information. The book contains a very brief outlined description of the application of the methods of electro-chemistry to the preparation of alkali and the various metals, and covers such a wide ground that it would be unreasonable to expect in it a great attention to detail. The author is somewhat given to making sweeping statements, the truth of which can hardly be accepted; for example, he is exceedingly sceptical about the use of electro-chemical methods in the preparation of organic products; in fact, he goes so far as to say that organic and electro-chemistry are as unmixable as oil and water, and instances the manufacture of iodoform as practically the only organic electro-chemical industry of Germany, thus quite passing over the preparation of the by-products of the coal-tar colours, naphthylamine, &c., which are now largely produced by electrical methods. Another error has crept into the chapter dealing with electrical bleaching, of which industry Kellner cannot be said to be the founder, for Hermite was undoubtedly the pioneer in this particular branch, and patented his process six or seven years before Kellner.

Die Materialien der Stereochemie. ("The Materials of Stereo-chemistry"). By C. A. BISCHOFF. Two Vols. Braunschweig: Friedrich Vieweg und Sohn. 1904.

THE collection of all data relating to the study of stereochemistry in this form is an excellent idea, and will commend itself to all who have occasion to look up any questions dealing with the subject. The text is arranged in the form of yearly reports extending from 1894 to 1902

inclusive, the preceding period being contained in the "Handbuch der Stereochemie," by C. A. Bischoff and P. Walden, to which these volumes may be regarded as a sort of enlarged supplement, and in each report the subject-matter is conveniently divided under the headings General Stereo-chemistry, Optical Isomerism, Geometrical Isomerism of Optically Inactive Substances, and the Relations between Spatial Arrangement and Chemical Reactions. Under these divisions books relating to each branch of the subject are noticed, and their contents given with a short review of points of special interest treated in them, and important papers which have appeared in various periodicals are very clearly abstracted. It is a pity, however, that preference is given so decidedly to works published in Germany only. The whole work is most admirably indexed, and the contents are so classified as to add greatly to the value and convenience of the book.

Flüssige Kristalle. ("Liquid Crystals"). By Dr. O. LEHMANN. Leipzig: Wilhelm Engelmann. 1904.

The author of this exhaustive treatise has boldly shaken himself free of all the trammels of theories relating to the three distinct states of aggregation, and attacks the questions of the existence of liquid crystals from the point of view of experimental observation alone. In this book, which is undoubtedly the most complete dealing with this subject extant, Dr. Lehmann, with all the vivacity and dexterity at his command, examines into the conceptions underlying the words liquid and crystal in order to justify their joint application to the well-known phenomena of anisotropic liquids, and gives a most complete statement of his case with all opposing arguments well threshed out. He describes very minutely the experimental arrangements adopted for the microscopic investigation of the phenomena in question, and appends to the text some beautifully executed photographs illustrating the various points in the treatise. In the short conclusion the application to biological problems is very briefly stated. Dr. Lehmann is perhaps rather disposed to over-estimate the importance of the discovery of the existence of liquid crystals and of the directive effects of molecular forces, which, in spite of what he says, has received a very fair amount of attention both from investigators and in text-books of physics; however, he has produced a valuable monograph on a very interesting subject.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 4, July 25, 1904.

The Form taken by Thallous Iodide when going into Solution.—D. Gernetz.—The author has already shown that when yellow thallous iodide is heated to 168° it is transformed into the cubic red iodide. The inverse reaction also takes place. He now proves that, at temperatures lower than 168°, if a solution of either form is made in any solvent whatsoever, and then—either by cooling or evaporation of the solvent—crystallisation takes place, the red variety, which is naturally unstable at these temperatures, always separates out.

Radio-active Lead, Radio-tellurium, and Polonium.—A. Debieuvre.—Already inserted in full.

Action of Zinc on Sodium Tungstates.—L. A. Hallopeau.—The author examines the reaction of zinc on neutral sodium tungstate, $\text{Na}_2\text{WO}_3 \cdot 2\text{H}_2\text{O}$, and sodium paratungstate, $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$. The latter can easily be prepared pure from commercial sodium tungstate. He finds that in the latter case the reaction is totally

different from that when the ammonium salt is used. The zinc first reduces a portion of the tungstic anhydride of the acid sodium tungstate. This first reaction gives the golden-yellow tungsto-sodic tungstate, and, in certain cases, a little tungsten. The oxide of zinc and the neutral sodium tungstate which are thus formed mutually react on each other to form the neutral zinc tungstate.

Acid Silver Pyrophosphate.—J. Cavalier.—The author prepares acid silver pyrophosphate by dissolving neutral silver pyrophosphate in pyrophosphoric acid. The mass when cooled is a thick syrup, which does not crystallise, but gives with alcohol or ether the acid pyrophosphate of silver, $\text{P}_2\text{O}_7\text{Ag}_2\text{H}_2$, in the form of a white powder, crystalline if the deposition is made slowly. The salt becomes pasty at 150°, and is quite liquid at 240°, and at this point begins to slowly decompose, losing water and turning into the metaphosphate, PO_3Ag . It is rapidly decomposed by water in the cold: $2\text{P}_2\text{O}_7\text{Ag}_2\text{H}_2 + \text{H}_2\text{O} = \text{P}_2\text{O}_5\text{Ag}_2 + \text{P}_2\text{O}_5\text{H}_2$.

Composition of the Homologues of Schweinfurt's Green.—Georges Viard.—The author prepares and analyses the formic, propionic, and butyric homologues of Schweinfurt's green. These are obtained by adding to a boiling aqueous solution of arsenious anhydride the solution of the organic salt of copper added to an excess of its acid. On continuing the boiling the substance separates in green crystalline flakes. These are very stable. The formio-arsenite of formula $(\text{CHO})_2\text{Cu} \cdot 3(\text{AsO}_2)_2\text{Cu}$ not decomposing at 170°, whilst the propiono-arsenite, $(\text{C}_3\text{H}_5\text{O}_2)_2\text{Cu} \cdot 3(\text{AsO}_2)_2\text{Cu}$, and the butyro-arsenite, $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Cu} \cdot 3(\text{AsO}_2)_2\text{Cu}$, only decompose at temperatures above 200°.

Heat of Formation of Antimony Trisulphides.—MM. Guinchant and Chretien.—The authors' number for the heat of formation of antimony trisulphide differs from that given by M. Berthelot. They explain this difference by the fact that the red sulphide which intervenes is not identical in the two methods.

Scientific Phenomena accompanying Polishing.—F. Osmond and G. Cartaud.—The authors explain and illustrate a theory of glass cutting by means of a diamond and various phenomena connected with polishing.

Vinyldimethylacetic Acid.—E. E. Blaise and A. Courtot.—Vinyldimethylacetic acid is the same as that to which M. Bouveault gives the name dimethylisocrotonic acid. Its constitution is absolutely proved by its oxidation by means of potassium permanganate. When this oxidation takes place at 0° in dilute solution the yield of dimethylmalonic acid is small, but in a 5 per cent solution (the temperature being higher) a good yield is produced. True vinyldimethylacetic acid when treated with sulphuric acid does not give lactone.

β -Oxalacetyl and β -Oxyphenol Ethylenic Acetones. Action of Hydroxylamine and Hydrazine.—Ch. Moureu and M. Brachin.— β -Oxalacetyl- and β -oxyphenol-ethylenic acetones, when reacting upon hydroxylamine and hydrazine, do not give directly either oximes or hydrazones, as is generally the case, but isoxazols and pyrazols are formed instead.

Action of Oxalacetic Ether on Aromatic Aldehydes in presence of β -Naphthylamine.—L. J. Simon and A. Conduché.—The authors find that, when oxalacetic ether acts on aromatic aldehydes in presence of β -naphthylamine, the principal product of the reaction results from the equimolecular addition of ether and the benzyldienic combination,

$$\text{CO}_2\text{C}_2\text{H}_5 \cdot \text{CO} \cdot \text{CH} \cdot \text{CO}_2\text{C}_2\text{H}_5$$

$$\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{C}_2\text{H}_5$$

Action of Acid Chlorides on Tertiary Bases having an Aromatic Radicle.—V. Auger.—The author finds that, at a temperature of 200° to 250°, all the acid chlorides act on the tertiary bases of the type $\text{Ar} \cdot \text{N} = \text{Al}_1\text{Al}_2$, and give an acyl-derivative in quantitative yield:— $\text{Ar} \cdot \text{N} : \text{Al}_1\text{Al}_2 + \text{ROCl} = \text{Ar} \cdot \text{N} \cdot \text{Al}_1 \cdot \text{COR} + \text{Al}_2\text{Cl}$. Al_1 representing the radicle possessing the lowest molecular weight.

No. 5, August 1, 1904.

Synthesis of certain Alcohols in the Cyclohexane Series.—Paul Sabatier and Alph. Maihe.—By applying M. Grignard's methods to a chloro-magnesium derivative of cyclohexane, the authors are enabled to synthesise other series of alcohols represented by the general formula $C_6H_{11}-COH \leftarrow \begin{smallmatrix} R \\ R' \end{smallmatrix}$; where R and R' can be hydrogen or hydrocarbon residues of various forms.

Action of Ammonia on Boron Bromide and Phosphorus Chloride.—A. Joannis.—When dry ammonia acts on boron bromide at about -10° a decomposition takes place, boron imide and ammonium bromide being formed. If the reaction takes place at 0° , the ammoniacal ammonium bromide is formed according to the equation $2BBr_3 + 27NH_3 = 6(NH_4Br_3NH_3) + B_2(NH_3)_3$. The author then causes ammonia to act on phosphorus chloride by passing the vapour of the latter by means of a stream of hydrogen into liquefied ammonia at -78° . In spite of this low temperature he is not able to obtain the amide $P(NH_2)_3$, but either a mixture of amide and imide, or, more usually, a body of formula $NH=P-NH_2$ is produced. When the reaction is finished, the excess of ammonia is evaporated at -23° , and there remains only the ammonia combined with ammonium chloride and the body above referred to: $PCl_3 + 14NH_3 = 3(NH_4Cl \cdot 3NH_3) + NH=P-NH_2$.

Estimation of Bismuth by Electrolysis.—A. Holland and L. Bertiaux.—The authors describe a method by which a very exact estimation of bismuth may be made, even in the presence of considerable quantities of copper and lead. This consists in obtaining the metals in the state of sulphate not containing a large excess of H_2SO_4 . They are then precipitated, when boiling, by excess of phosphoric acid. The precipitate is left to settle overnight. Next day it is filtered and washed with dilute phosphoric acid and then with ammonium sulphohydrate and potassium cyanide. The precipitate of bismuth phosphate is dissolved in dilute nitric acid and the solution evaporated in presence of sulphuric acid till white fumes appear. The bismuth is now in the state of pyrophosphate; this is diluted and electrolysed with a current of 0.1 ampère, when the bismuth absolutely separates.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xxxvii., No. 12, 1904.

Oxidation Products of β -Phenylene Diamine.—Ernst Erdmann.—The oxidation of β -phenylene diamine has for some time been known to produce brown and black colours, and this property has found practical application in colouring skins, &c. In this first communication the author describes his investigations of these oxidation products, produced by the action of permanganate. Using a solution of chemically pure β -phenylene diamine, a 1 per cent solution of permanganate is appreciably decolourised in the cold. The molecule of diamine is split up, most of the nitrogen being converted into ammonia; a small part of it (about 1 per cent of the diamine used) goes to form hydrocyanic acid. The formation of this latter product may be the explanation of the toxicological effects of the diamine. Possibly isonitroso-malonic acid is formed as an intermediate product, which readily splits up into carbon dioxide, hydrogen cyanide, and water. Oxalic acid is also formed during the oxidation, but both this and hydrocyanic acid are only secondary products, the principal reaction giving rise to CO_2 and NH_3 , and proceeding according to the reaction $C_6H_8N_2 + 13O = 6CO_2 + 2NH_3 + H_2O$.

Removal of Alkyl Groups from Secondary Amines.—J. von Braun.—The author discovered some time ago that tertiary amines, R_3N , by means of the bromocyanogen reaction could be made to yield dialkyl cyanamides, $R_2N.CN$, which practically amounts to converting tertiary into secondary bases. He has now found a method of further decomposing secondary amines so as to remove the alkyl residue R, so that we can obtain a given nitrogen

atom with any desired number of alkyl residues attached to it. If dialkyl amides which contain a benzene, substituted benzene, or naphthalene residue are converted into amide chlorides, and heated, or if, more simply, PCl_5 is allowed to act on the amide (in molecular proportions) 1 molecule of alkyl chloride is split off on heating for a short time, and on heating for a longer time to a higher temperature the second molecule of alkyl chloride is eliminated. If one of the two alkyl residues attached to the nitrogen is aromatic, the reaction obviously consists of the splitting off of a molecule of fatty alkyl chloride, and the formation of the double aromatic imide chloride (e.g., $C_6H_5.CCl.N.C_6H_5$). Secondary fatty bases can thus be decomposed to form ammonia, and fatty aromatic bases to primary aromatic bases: $R_1CCl_2.NR_2 = R_1CCl.NR + ClR$, $R_1CCl_2.NR_2 = R_1C.N + 2ClR$. Though of only theoretical interest, this reaction is of importance when applied to aromatic acylid derivatives of cyclic bases, for it leads to a new method of splitting up nitrogenous rings, and to a series of substances hitherto only prepared with great difficulty, and applicable for further syntheses.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemistry) at the Cambridge Meeting of the British Association:—

President.—Prof. Sydney Young, D.Sc., F.R.S.
Vice-Presidents.—Prof. Sir James Dewar, M.A., LL.D., F.R.S.; Prof. W. N. Hartley, D.Sc., F.R.S.; J. J. Dobbie, D.Sc., F.R.S.

Secretaries.—Prof. W. J. Pope, F.R.S. (Recorder); M. O. Forster, Ph.D., D.Sc.; Prof. G. G. Henderson, M.A., D.Sc.; H. O. Johns, M.A., D.Sc.

Committee.—John Angell; Prof. H. E. Armstrong, F.R.S.; Prof. O. Aschan; William Barlow; G. T. Beilby; Sir I. Lowthian Bell, F.R.S.; J. Carter Bell; Prof. J. Brühl; J. Y. Buchanan, M.A., F.R.S.; Prof. M. Busch; F. D. Chattaway, M.A., D.Sc.; Holland Crompton; Prof. A. W. Crossley, Ph.D., D.Sc.; Prof. C. Dieterici; Prof. H. B. Dixon, F.R.S.; Prof. A. E. Dixon, M.D.; A. Etard, D.Sc.; T. Fairley; H. J. H. Fenton, F.R.S.; Prof. Ferguson, M.A., LL.D.; Prof. A. P. N. Franchimont; Prof. M. Freund; Prof. S. Gabriel; Comte A. de Gramont; Prof. Groth; Prof. P. Guye; Prof. A. Haller; A. Vernon Harcourt, D.C.L., F.R.S.; M. Hayashi, D.Sc.; C. T. Heycock, F.R.S.; J. Hübner; Francis Jones; Prof. E. Knoevenagel; A. Lapworth, D.Sc.; Prof. Leduc; Prof. G. D. Liveing, F.R.S.; Prof. A. Liversidge, F.R.S.; H. McLeod, F.R.S.; H. Marshall, F.R.S.; K. Matsubara, Ph.D.; Prof. R. Meyer; H. Forster Morley, D.Sc.; R. S. Morrell, M.A.; M. M. Pattison Muir, M.A.; F. H. Neville, F.R.S.; E. Noelting; M. Ogawa; Prof. K. J. P. Orton; H. Ramage, M.A.; Sir W. Ramsay, K.C.B., F.R.S.; Prof. J. E. Reynolds, M.D., F.R.S.; Prof. P. van Romburgh; Sir H. E. Roscoe, F.R.S.; S. Ruhemann, Ph.D.; H. Rupe, Ph.D.; A. Scott, F.R.S.; W. J. Sell, F.R.S.; W. A. Shenstone, F.R.S.; Prof. A. Smithells, F.R.S.; J. Smyth; Prof. J. J. Sudborough, D.Sc., Ph.D.; W. Thomson; T. E. Thorpe, C.B., F.R.S.; Prof. I. Traube; Prof. P. Walden; Sir Thomas Wardle, F.G.S.; Prof. E. Wedekind; Prof. R. Wegscheider; Prof. R. Wolfenstein; Dr. A. Harden; Dr. A. Hutchinson.

The papers brought before the Section were as follows:—

- President's Address.**
Prof. C. Dieterici.—Energy of Water and Steam at High Temperatures.
G. T. Beilby.—Relation between the Crystalline and the Amorphous States as disclosed by the Surface Flow of Solids.
G. T. Beilby.—Action of certain Gases on Glass in the Neighbourhood of Hot Metals.

- C. T. Heycock and F. H. Neville—Methods of Investigating Alloys Illustrated from the Copper-tin Series.
Prof. A. W. Crossley—Hydro-aromatic Compounds.
W. J. Sell—A Hexachlor- α -picoline and its Derivatives.
P. V. Bevan—Change of Conductivity in Solutions during Chemical Reactions.
F. G. Doman—Suggested Explanation of the Phenomena of Opalescence observed in the Neighbourhood of Critical States.
Major A. E. Edwards and Prof. W. R. E. Hodgkinson—On Double Acetylides.
Prof. W. R. E. Hodgkinson and A. H. Coote—On some Reactions between Ammonium Salts and Metals.
Prof. P. Groth—Crystal Structure and its Relations to Chemical Constitution.
T. M. Lowry—Dynamic Isomerism.
Prof. Richard Meyer—Constitution of Phthalein Salts.
R. S. Morrell and E. K. Hanson—Studies in the Dynamic Isomerism of α - and β -Crotonic Acids.
H. J. H. Fenton—Mesoxalic Semialdehyde.
H. J. H. Fenton—Influence of Radium Radiations on Atmospheric Oxidation in presence of Iron.
H. J. H. Fenton and J. P. Millington—Colour Reaction for Methylfurfural and its Derivatives.
H. J. H. Fenton—A Reaction for Ketoses.
Prof. H. B. Dixon—Specific Heat of Gases at High Temperatures.
R. S. Morrell and A. E. Bellars—Oxidation of Carbohydrates by Hydrogen Peroxide in presence of Ferrous Sulphate.
C. T. Heycock and F. H. Neville—Demonstration on the Structure of Metals and on Platinum Resistance Pyrometry.
M. le Comte de Gramont—Sur le spectre du soufre dans la photographie de l'étincelle des minéraux.
Sir William Ramsay—Changes produced by the β -Rays.
H. O. Jones—Stereochemistry of Nitrogen.
Prof. Ossian Aschan—On the Pentavalent Nitrogen Atom.
Prof. E. Weckind—The Asymmetric Nitrogen Atom.
(The last three communications formed the basis of a Discussion on the Stereochemistry of Nitrogen).
Prof. E. Weckind—Products obtained by the Action of Tertiary Bases on some Acid Chlorides.
Dr. A. Etard—Sur les manganates et les permanganates.
W. Achroyd—Bearing of the Colour Phenomena presented by Radium Compounds.
Prof. R. Wolfenstein—Pseudomorphism in Organic Persulphates.
Prof. G. J. Stokes—A New Theory of the Periodic Law.
M. le Comte de Gramont—Quelques observations sur le groupement des raies du spectre du silicium d'après l'effet de la self-induction, et sur leur présence dans les spectres stellaires.
Prof. I. Traube—On the Velocity of Osmosis and on Solubility: a Contribution to the Theory of Narcosis.
Dr. S. Ruhemann—The Action of Organic Bases on Olefinic Ketonic Compounds.
Dr. W. A. Bone and R. V. Wheeler—The Union of Hydrogen and Oxygen in Contact with a Hot Surface.
Dr. E. P. Perman—The Decomposition and Synthesis of Ammonia.
D. L. Chapman and C. H. Burgess—The Active Variety of Chlorine.
Prof. Isidor Traube—Exhibition of Effects produced by Precipitating Silver Chromate in Gelatin.
Prof. A. Liversidge—Exhibition of Photographs of Sections of an Australian Siderite.
Prof. S. Gabriel—Ueber Isocystein (Isothioserin).
Dr. G. Barger—Saponarin: a Glucoside Coloured Blue by Iodine.
Dr. A. Scott—Vapour Density of Hydrazin Hydrate.
Dr. A. Scott—The Combining Volumes of Carbon Monoxide and Oxygen.
Dr. A. Scott—Action of Heat on Oxalates.
Dr. A. Scott—Some Alkyl Derivatives of Sulphur, Selenium, and Tellurium.

W. Thomson—Presence of Arsenic in the Body and its Secretion by the Kidneys. (With an Exhibit of Apparatus).

Prof. Sir James Dewar—On New Low Temperature Phenomena and their Scientific Applications.

Ozone Considered as an Oxidising Agent.—R. Luther and J. K. H. Inglis.—The authors have observed that after an electrolysis, the liquid near to the anode has a considerable oxidising power; a supplementary platinum electrode plunged into this liquid and connected with a normal calomel electrode forms an element having an electromotive force of about 1.1 volts. This phenomenon cannot be attributed to dissolved oxygen or to peroxide of hydrogen, the value of their oxidation potential not agreeing with the figure thus found. This value of the electromotive force being found as well in the electrolysis of NO_2H or PO_4H_3 as in H_2SO_4 , there can be no question of persulphuric acid or of Caro's acid, as the authors supposed at first. Finally, the phenomenon disappears in alkaline solutions. For all these reasons they have come to the conclusion that its production is due to the oxidising action of the dissolved ozone. Experiments having confirmed this opinion, the authors undertook the systematic examination of the potential of oxidation of ozone dissolved in acid solutions. They have observed that in contact with electrodes of polished platinum, ozone gives rise to an electromotive force which, at a given temperature, depends on its concentration and on that of the H ions, and can be determined to about 1 millivolt. The potential of oxidation of the electrode is lowered if the former is previously charged with oxygen, and it is increased if it is previously charged with hydrogen; we can prevent these causes of error by first plunging the electrode into an acid solution of ferroso-feric salts, which practically frees it from both these gases. The authors give the formulæ by which we can calculate the electromotive force of a platinum-ozone electrode in functions of the concentration of the ozone and of the H ions; also that of an ozone-hydrogen cell, at $+2^\circ$, in functions of the concentration of the ozone. They are led to the conclusion that ozone might be the anhydride of a weak acid, of which the formula would be H_2O_7 or H_2O_8 . They observed finally that the action of ozone in acid solution on iodide of potassium in neutral solution sets free three atoms of iodine per molecule of ozone; in neutral solutions two atoms of iodine only are set free. In the same manner the action of ozone on a ferrous salt, in neutral solution, oxidises two molecules of ferrous salt per molecule of ozone.—*Zeit. Physik. Chem.*, vol. xliii., p. 203.

COUNTY OF LONDON.

To LIME MERCHANTS, MANUFACTURING CHEMISTS, AND OTHERS.

The LONDON COUNTY COUNCIL invite

Tenders for the Supply of—

- 23,800 Tons of LIME, and
- 5,550 Tons of PROTOSULPHATE OF IRON (Commercial Green Vitriol)

to the Barking Outfall Works, near Beckton, North Woolwich, and the Crossness Outfall Works, near Erith, Kent.

Forms of Tender and other particulars may be obtained upon application to the Council's Chief Engineer, Mr. MAURICE FITZMAURICE, C.M.G., at the County Hall, Spring Gardens, S.W.

Each Tender, which must be upon the Official Printed Form and comply with the instructions contained therein or be rejected, is to be delivered at the County Hall, in a sealed cover marked "Tender for Lime" or "Tender for Protosulphate of Iron" and addressed to the Clerk of the London County Council, not later than 10 o'clock a.m. on TUESDAY, the 4th day of OCTOBER next.

The Council does not bind itself to accept the lowest or any Tender, and it will not accept the Tender of any person or firm who shall on any previous occasion have withdrawn a Tender after the opening of the same, unless the reasons for the withdrawal were satisfactory to the Council.

G. L. GOMME,
Clerk of the London County Council.
The County Hall, Spring Gardens, S.W.,
September 2nd, 1904.

THE SIR JOHN CASS TECHNICAL INSTITUTE.

JEWRY STREET, ALDGATE, E.C.

Principal—CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.

EVENING CLASSES IN CHEMISTRY, METALLURGY, PHYSICS, and MATHEMATICS.

Designed to meet the requirements of those engaged in CHEMICAL, METALLURGICAL, and ELECTRICAL INDUSTRIES,

and in trades associated therewith.

Also preparation for the B.Sc. Examination of London University.

Every facility for Special and Advanced Practical Work in well-equipped Laboratories, both in the Afternoon and Evening

CHEMISTRY	{ CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.
PHYSICS	{ R. S. WILLOWS, D.Sc., M.A.
METALLURGY	{ C. O. BARNISTER, Assoc. R.S.M.
MATHEMATICS	{ G. M. K. LEGGETT, B.A.

CLASSES IN METALLURGY.

GENERAL METALLURGY.

THE METALLURGY OF GOLD, SILVER, and LEAD.

FUEL and REFRACTORIAL MATERIALS.

METALLOGRAPHY, including PYROMETRIC WORK.

ASSAYING.

ANALYTICAL CHEMISTRY.

Including ELECTROLYTIC and GAS ANALYSIS.

Each Course of Lectures will be accompanied by suitable Laboratory Work.

GLASS BLOWING.

A series of Courses of Instruction will be given during the Session by Mr. A. C. COSSOR.

New SESSION begins MONDAY, SEPT. 26th,

The Institute is readily accessible, and near to Fenchurch Street, Liverpool Street, Broad Street, and Metropolitan Railway Stations.

For details of the Classes apply at the Office of the Institute, or by letter to the PRINCIPAL.

W. H. DAVISON, M.A.,
Clerk to the Governing Body.

THE POLYTECHNIC,

309, REGENT STREET, W.

UNIVERSITY OF LONDON PREPARATION CLASSES.

Full Courses of Instruction for Matriculation, Inter. Arts, Science, and Engineering, and Final Arts. Examinations are held at the above Institute.

NEXT TERM commences SEPTEMBER 16th, 1904.

Courses are so arranged that Students can do the work on Saturday and one evening per week.

Full particulars can be obtained on application to the DIRECTOR OF EDUCATION.

CITY OF LONDON COLLEGE,

WHITE STREET and ROPEMAKER STREET,
MOOKFIELDS, E.C.

MICHAELMAS TERM commences OCTOBER 3rd.

CLASSES and LABORATORY WORK in CHEMISTRY, PHYSICS, BIOLOGY, BOTANY, GEOLOGY, and PHYSIOLOGY. Special preparation for the Examinations of the Pharmaceutical Society, The Conjoint Board. Complete Courses for University Matriculation and Inter. and Final B.Sc., meeting during the Evening and on Saturday.

Full particulars gratis on application to—

DAVID SAVAGE, Secretary.

REDRUTH SCHOOL OF MINES, CORNWALL.

Session 1904-1905 begins September 7th.

A "Mining Certificate" is awarded to Students passing successfully through the School Course.

PRACTICAL MINING CLASSES, under the Instruction of Capt. WILLIAM HANLEY (late Government Inspector, South Africa). Distinctions in Mine Surveying in Open Examination five years in succession, including five Medals and Prizes, being all the awards of the City and Guilds of London Institute in 1904 in this subject.

SYLLABUS and every information on application to—

THE REGISTRAR.



RADIUM BROM.

POLONIUM.

RADIO-ACTIVE ORES.

BAR.-PLAT. CYAN. SCREENS.

LARGE CRYSTALS.

ETC., ETC.,

ALL AT REASONABLE PRICES.

Armbrecht, Nelson & Co.,

71-73, Duke-st., Grosvenor-sq., W.

'Phone—1942 Gerard.

BIRKBECK COLLEGE

(BIRKBECK INSTITUTION),

Breams Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.

METALLURGY, MINING, and ASSAYING G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board, Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.



OLD PLATINUM

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and Purchased.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC,

As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, SHOT, &c.

THE CHEMICAL NEWS.

VOL. XC., No. 2337.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; one commencing on September 12th, one on the second Monday in January, and the third on the second Monday in June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following five subjects:—(1) English; one paper of three hours. (2) Elementary Mathematics; two papers of three hours each. (3) Latin or Elementary Mechanics, or Elementary Physics—Heat, Light, and Sound, or Elementary Chemistry, or Elementary Botany; one paper of three hours in each subject. (4) and (5) Two of the following subjects, neither of which has already been taken under Section (3); one paper of three hours in each subject; if Latin be not taken, one of the other subjects selected must be another Language from the List, either ancient or modern:—Latin, Greek, French, German, Arabic, Sanskrit, Spanish, Portuguese, Italian, Hebrew, Ancient History, Modern History, Logic, Physical and General Geography, Geometrical and Mechanical Drawing, Mathematics (more advanced), Elementary Mechanics, Elementary Chemistry, Elementary Physics—Heat, Light, and Sound, Elementary Physics—Electricity and Magnetism, Elementary Biology—Botany, Elementary Biology—Zoology. Candidates in subjects marked with asterisk must give at least two months' notice before the commencement of the Examination.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Several valuable Scholarships and Exhibitions are available to students.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year, once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.
Lees Reader in Chemistry—G. Brereton Baker, M.A.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £80 are obtainable

at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Emmanuel, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.
Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.
Demonstrator—W. C. Ramsden, F.C.S.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced, including Physical Chemistry, second year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Freshmen, and tenable for five years. These Foundation Scholars receive £20 per annum, have free commons, their chambers for half the charge paid by other students, and their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(DIVISION OF ENGINEERING, ARCHITECTURE, AND APPLIED SCIENCE).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.
Lecturer—Herbert Jackson, F.C.S.

Demonstrators—P. H. Kirkaldy, F.C.S., Dr. Northall Laurie, F.C.S., and Sir W. Collins.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1904-1905 are Oct. 5, Jan. 9, and May 1.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *visà voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s.; per ann., £8 8s.; Practical Chemistry per term, £4 4s.; per ann., £10 10s.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.
In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professors—Sir William Ramsay, LL.D., F.R.S., &c. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—E. C. C. Baly, F.I.C.; J. K. H. Inglis, B.Sc., M.A.; N. T. M. Wilmore, M.Sc.; and S. Smiles, D.Sc. The Session is divided into three Terms, as follows:—First Term, from October 4 to December 22; Second Term, from January 10 to March 31; Third Term, from May 2 to June 19. Class Examinations begin June 19.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Friday, 2 to 2.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; for the First or Second Terms, £4 4s.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds are treated in considerable detail, under the headings—Elements; halides, oxides, sulphides, &c., borides, carbides, and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

An Exercise Class will meet once a week throughout the Session.

Senior Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning in January.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent Chemical Theory researches.

Third Term: Some Lectures will also be given on Saturdays at 9, during the Third Term, on the History of Chemistry.

Organic Chemistry.

Mondays, Wednesdays, and Fridays, at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the preceding Course, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

An Advanced Course will be held twice a week during the First, Second, and third Terms, for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

ROYAL COLLEGE OF SCIENCE AND
ROYAL SCHOOL OF MINES.

Professor of Chemistry—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—M. O. Forster, Ph.D., D.Sc.

Demonstrators—H. Chapman Jones; G. T. Morgan, D.Sc., A.R.C.S.; and J. C. Philip, M.A., Ph.D., B.Sc.

Assistants—G. S. Newth and H. Burrows, Ph.D.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Board of Education. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction lasts for three years, is the same for all the divisions during the first year, after which it is specialised according to the particular division in which the student is working for the Associateship.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject except Mining and Metallurgy and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the dis-

cretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy .. .	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	

The fee for the course of Mine Surveying is £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

The Session is divided into two Terms. The first Term begins about the first week of October, and ends about the middle of February. The second Term begins in the middle of February, and ends about the middle of June.

The hours of study are from 10 a.m. to 1.15, and from 2 to 4 or 5 p.m. every day, except on Wednesday and Saturday, when the College closes at 1 p.m.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-third Session will commence on Oct. 3, 1904.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C.; Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Pharmacaceutics, Henry G. Greenish, F.I.C., F.L.S., (Dean).

A course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Demonstrators—H. Hibbert, M.Sc. (Vic.), F.I.C., and A. Brooke, Ph.D. (Strassburg).

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

Lecturer on Dyeing—(Vacant).

The College is open to male and female students above the age of sixteen years. The Session commences on Oct. 4th, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly throughout the Session. (2) Intermediate Science Course; four lectures weekly throughout the Session. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1904-1905, Course B). (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES. *Chemistry.*—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturer and Demonstrator, Alexander Lauder, B.Sc., F.C.S. Assistant Lecturer in Agricultural Chemistry, Alan Baguley, B.Sc., F.I.C. Junior Demonstrator, Edward Jones, B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 4th, 1904. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

**UNIVERSITY COLLEGE OF SOUTH WALES
AND MONMOUTHSHIRE, CARDIFF.**

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Demonstrator—R. D. Anell, D.Sc.

The Session commences October 14th, and terminates on June 23rd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Morris W. Travers, D.Sc., F.R.S.

Assistant Professor—Francis E. Francis, D.Sc., Ph.D.

Lecturer—Oliver C. M. Davis, B.Sc., A.I.C.

Lecture Assistant—J. H. Sturges

The session 1904-1905 will begin on October 4. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Elementary Course.—Three Lectures a week will be given during the Session. Fee, £3 13s. 6d.

Special Course.—A special course of Lectures is also given to Elementary Teachers.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Advanced Course.—Two Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Organic Chemistry.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d. An advanced course of lectures will also be given one day a week during the session. Fee, £2 2s.

Practical Chemistry.—Laboratory Instruction.

The Chemical and Metallurgical Laboratories will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

EVENING LECTURES.

A course of Lectures, which is subject to variation to suit the requirements of Students, will be delivered during the First and Second Terms. Fee 7s. 6d.

Pharmaceutics.—During the first and second Terms a course of Lectures will be given one evening a week dealing chiefly with the *Materia Medica*, Pharmacy, and Chemistry of the British Pharmacopoeia. Fee, £1 1s.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open one evening a week from 6 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—Two Terms, 21s.; One Term, 12s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY AND METALLURGY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Lecturers—G. P. Darnell Smith, B.Sc., F.I.C., F.C.S.; H. A. M. Borland, A.R.C.S.; I. Williams, B.Sc.

Demonstrators—E. H. T. Parker; P. W. Alloway; C. D. Fuller.

Assistants in Chemical Laboratory—E. H. Fray, H. M. Spencer.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (for forty Students working at one time), Senior Laboratory, Gas Analysis Room, Balance Room, Combustion Room, Store Rooms, Metallurgical Laboratory, and Research Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Principal; and the Courses provide completely for the Preliminary Scientific Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. degree of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute, provided the details in each case be certified by the Professors.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 to 15s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Evening Classes, available to persons of either sex, will commence on Monday, September 26th.

Further detailed information may be obtained from the College Prospectus, price 6d.

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S.

Assistant Lecturers and Demonstrators—Alex. McKenzie, M.A., D.Sc., Ph.D.; Alex. Findlay, M.A., D.Sc., Ph.D.; T. S. Moore, B.A.

The Session will be opened on October 3rd, 1904.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. Mondays to Thursdays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—**Advanced Organic Chemistry.**—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. **General and Physical Chemistry.**—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General and Physical Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms ..	13	8½	7½	5
Three Terms ..	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of about £96 is awarded annually in September.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham

in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

DEPARTMENT OF CHEMISTRY AND DYEING.

Head of Department—Prof. W. M. Gardner.

Lecturers in Chemistry—B. North, A.R.C.Sc. (Lond.);

L. L. Lloyd, Ph.D.; S. F. Stell, F.C.S.

Demonstrators in Chemistry—A. H. M. Wheatley and G. Sargent.

Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).

Demonstrator in Physics—E. B. Walker.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Demonstrator in Dyeing—L. Min kin.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer on Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over four years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Extending over one or two years.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.)*, London.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

IX. Attendance at the College Courses and College Certificates in Chemistry, Physics, Animal Biology, and Botany are recognised by the Conjoint Board for Medical Studies.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in

the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.
Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc.

Assistant Lecturers and Demonstrators—T. S. Patterson, Ph.D., and H. M. Dawson, B.Sc., Ph.D.

Demonstrators—C. E. Whiteley, M.Sc., and W. Lowson, B.Sc., F.I.C.

The Session begins October 5, 1904.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Honours Courses—

(a) Organic Chemistry.—Monday, Wednesday, and Friday at 12 noon in the First and Second Terms. Fee, £2 12s. 6d.

(b) History of Chemistry.—Monday, Wednesday, and Friday at 9.30 a.m. in the First Term. Fee, £1 11s. 6d.

(c) Physical Chemistry.—Tuesday, Thursday, and Saturday at 9.30 a.m. in the Second and Third Terms. Fee, £2 12s. 6d.

(d) Electro-chemistry.—One hour weekly. 31s. 6d.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from January to March. Fee, £5 5s.

Elementary Science for Teachers.—Saturdays, 9.30 to 12.30, for half the session. £2 12s. 6d.

Dyeing and Tintorial Chemistry Department.

Professor—Arthur G. Green, F.I.C.

Lecturer and Research Assistant—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—A. B. Steven, B.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Assistant Lecturer and Demonstrator—F. Kopecky.

Demonstrator—Harold Brumwell.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the University, viz., the Salt, Akroyd, Brown, Baines, Emsley, Craven, Wheatley, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Demonstrators and Assistant Lecturers—A. T. de Moulpied, M.Sc., Ph.D.; A. W. Titherley, D.Sc., Ph.D.; B. C. Burt, B.Sc.; and F. J. Brislee, M.Sc.

Assistant—H. H. Froyssell.

The Session commences October 1st.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool, London, and Edinburgh; for the Pharmaceutical Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

A. General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Metals and Non-metals. Fee, £3.

Course C.—Inorganic Chemistry. Fee, £3.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Special Organic Subjects. Fee, £2.

Course F.—Physical Chemistry. Fee, £2.

Course G.—Advanced Physical Chemistry. Fee, £2.

Course H.—History of Chemistry and of Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses I.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electro-chemistry. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Preliminary. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Examination of Water and Air, &c.

Chemical Laboratory.

The Chemical Laboratories recently enlarged provide accommodation for every kind of chemical and metal-

lurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water Analysis, Gas Analysis, Photometry and Photography, Electro-chemical Work, Metallurgy Laboratories, a Research Laboratory, and a Museum. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

D.P.H. Course (see special syllabus).

Course for Dental Degree (see special syllabus)

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the University Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses B and D; Chemical Laboratory three days per week; Technological Chemistry, Course I. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Courses C and F, Technological Chemistry, Course I. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the B.Sc. Degree of the University of Liverpool, or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses G, H, and I. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses F, H, and I. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses F and I, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week.

Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1905, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15, 1905. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

The Prospectus containing particulars may be obtained from the Secretary, University of Liverpool.

**DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-ON-TYNE.**

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturer and Demonstrator—J. A. Smythie, M.Sc., Ph.D.

First Year Courses.—1. *General Course*.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 7 h. Fee, £3 10s. for the Session.

2. *Special Course*.—More advanced than the above. Wednesdays and Fridays, 11 to 12. Fee, £3 10s. for Session.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 6th. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, G. H. Stanley, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees*.—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subject professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in the following subjects:—

Arithmetic; English Essay; Geometry; the subject-matter of Euclid, Books I., II., III.; Algebra, up to and including Quadratic Equations. Also any two of the following:—English Language; Latin, including Grammar and Easy Sentences; Greek; French; German; Geography. The next examination commences on September 26. Names to be sent in at least ten days before this date. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—1. The first examination for the Degree of B. Litt. 2. Durham Examination for certificate of proficiency in General Education, held in March and September. 3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining, and passing the several examinations.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in September next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 26th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 26th. Candidates should send in their names to the Secretary on or before September 19th.

**OWENS COLLEGE,
THE VICTORIA UNIVERSITY OF MANCHESTER.**

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; D. L. Chapman, B.A.; Norman Smith, B.Sc.; F. V. Darbishire, B.A., Ph.D.; C. H. Burgess, B.Sc.

Demonstrator in Organic Chemistry—D. T. Jones, B.Sc. *Lecturer in Technical Organic Chemistry*—Jocelyn F. Thorpe, Ph.D.

Lecturer in Metallurgy—Dr. Bone. *Lecturer in Electro-Chemistry*—R. S. Hutto, B.Sc.

The Session begins on October 4, 1904.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.—*General Chemistry Course*.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Tuesdays, Thursdays, Saturdays, 11.30 a.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

CHEMICAL LABORATORIES.—These have again been extended. Two large rooms have been added to the main laboratories; one for Inorganic and one for Organic work. These will connect the present buildings to the Schunck Laboratory. The Laboratory and Chemical Library belonging to the late Dr. E. Schunck, F.R.S., left by him in 1902 for the use of the Owens College, has been re-erected in Burlington Street. The Schunck Laboratory is to be devoted to research work.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

METALLURGY.—*Lectures:* (A) The Metallurgy of Copper, Lead, Silver, Gold, Zinc, and Antimony; and (B) the Metallurgy of Iron and Steel.

The Metallurgical Laboratory, which is open every day in the week, has been greatly enlarged and re-equipped with a view to research work on the structure and properties of Steel and other Alloys, and the Chemistry of Fuel and Gases.

ELECTRO-CHEMISTRY.—In connection with the John Hopkinson Memorial Laboratory, rooms have been fitted for the study of Electricity in its applications to Chemistry. There is a complete equipment for Electro-chemical and Electro-metallurgical work. Demonstrator and Assistant Lecturer in Electro-technics, Robert Beattie, B.Sc. (Durham). Demonstrator and Assistant Lecturer in Electro-chemistry, R. S. Hutton, M.Sc. (Vic.).

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Matriculation Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry or Metallurgy Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £100 is awarded annually among the Graduates in Science for the encouragement of Research. Among the College Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship, &c.

Schunck Fellowship.—A Fellowship for Chemical Research will be offered during the Session 1904-5 under the Schunck endowment, a portion of the income arising from which is at present used for providing expensive material required in research work. Properly qualified Students may be appointed to Research Studentships, which entitle the holders to work in the laboratories under reduced fees.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff. For further particulars apply to the Registrar, Mr. S. Chaffers.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry.—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry.—R.M. Caven, D.Sc., F.I.C.; A. Sator, Ph.D., B.Sc.; and G. Sand, Ph.D., M.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 3rd, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh; they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given

in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 15s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.
Lecturer—G. Young, Ph.D., F.R.S.E.

The Session will commence on October 5th.

Matriculation Course.—Tuesday and Friday 10—11. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Intermediate Course.—Monday and Thursday, 10—11 a.m.; Saturday, 10—11 (2 Terms), £3 13s. 6d., and nine hours per week Laboratory work.

B.Sc. Course.—Monday, Tuesday, and Friday, 10—11, and another hour to be arranged, £5 15s. 6d., and twelve hours per week Laboratory work.

Organic Chemistry.—Elementary: Saturdays, 10—11, fee £1 1s. Advanced: Tuesdays and Fridays, 10—11, fee £2 12s. 6d.; Tuesdays and Fridays, 12—1, fee £2 12s. 6d.; another hour to be arranged, fee £1 11s. 6d.

Physical Chemistry.—Monday, 10—11, fee £1 11s. 6d.

History of Chemistry.—Tuesday, 11—12, fee £1 11s. 6d. A course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board of Education, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8—9. Laboratory instruction, Wednesday, 6—9. Sessional Fee, Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

DEPARTMENT OF METALLURGY

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students engaged in Collieries or Gas-Works.

A new steel works has recently been erected in connection with the Sheffield College at a cost of about £10,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works is also provided with a hammer capable of dealing with four-inch ingots. Differential annealing furnaces, oil-brightening and lead-tempering tanks will constitute part of the new plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, D.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 11th, and ends on March 15th. The Summer Session extends from the middle of April to the end of June.

The *Junior Lecture Course on Systematic Chemistry* is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.
Demonstrators—A. N. Meldrum, D.Sc., and John Alexander, M.A.

I. General Lecture Course (100 Lectures).—Daily during the Winter Session. The subjects treated of include (1)

The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Senior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry* (50 Lectures).—Daily during the Summer Session. Fee, £3 3s.

III. *Practical Course for Medical Students*.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £4 4s.

IV. *Chemical Laboratory*.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £4 4s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

V. *Physical and Advanced Inorganic Chemistry* (30 Lectures).—In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. A. N. Meldrum. Fee, £2 2s.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

This course is given during the Winter Session, and includes both Lectures and Laboratory work. The Lectures deal with the chemistry of the atmosphere, the soil, manures, and foods. The physiological chemistry of plants and animals, the composition and manurial requirements of crops, and dairy chemistry, are also treated of. The Laboratory work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of soils, manures, feeding stuffs and waters, and with the impurities and adulterations of these, occupy much of the time given to practical work. The fee for the whole course—lectures and practical work—is £4 4s.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. An Intermediate Course of Organic and Advanced Inorganic Chemistry is held in summer; fee, £2 2s. There is also a class on History of Chemistry or Chemical Theory, by Dr. Dobbin; fee £1 1s.; and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter

Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Physico-Chemical Measurements, Agricultural Chemistry, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-Chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—Bertram D. Steele, D.Sc.; Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; and Dr. Emil Westergaard.

The Session begins October 4th, 1904.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electro-chemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

Matriculation Fee, 5s.; Composition Fee for Engineering Courses, £12 12s. per Session; for Chemistry Courses, First Session, £12 12s.; Second Session, £12 12s.; Third Session, £15 15s.; Fourth Session, £15 15s. Full particulars are published in the Calendar of the College early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 27. Entrance Examination Sept. 19. The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1904-1905 may be had from Mr. H. F. Stockdale, Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.
Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 7th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for thirty-five Bursaries, ranging in value from £40 to £100 each per annum, will be held on September 23rd and following days. Nineteen of these Bursaries are restricted to Men, one to Men or Women, and fifteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and

Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Examinations, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—

(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s. and for the Advanced Course £5 5s.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable

for three consecutive years. Also a Junior Fellowship, tenable for four years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—Robert Elliott Doran, F.C.S.

The College Session will commence on October 18th, 1904, and end on June 10th, 1905. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be specially arranged as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1905.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics, First-class value £42, and Second-class value £21, together with other prizes, e.g., a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C., F.C.S.

Demonstrator—Miss Rosalind Clarke.

Research Assistants—W. Sloan Mills, M.A., and Percy C. Austin, B.A.

The College Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by three Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Professor of Chemistry—W. N. Hartley, F.R.S., D.Sc.

Lecturer on Organic Chemistry—(Vacant).

Senior Assistant—J. Holms Pollok, B.Sc.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, Agriculture, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships include free education for the full Associateship Course of three years and maintenance allowance of a guinea a week during the Session.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London,

E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net. — *City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 20th, and the Winter Session opens on Tuesday, October 4th. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 20th. Session begins October 4th. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics. Session commences Oct. 3rd.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh.Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vit.), assisted by Mr. John L. White, M.Sc., Mr. H. Evans, and others. Session opens Sept. 26. Complete courses of instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Paper Testing, Paper Making, Gas Manufacture, Gas Analysis, Oils, Fats, and Soaps, Chemistry of Building Materials, Chemistry of Foods, &c.

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. J. E. Mackenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. This Institution, which has now completed eighty-one years of educational work in the metropolis, com-

mences its new Session on Monday, October 3, when an opening address will be delivered by Dr. J. E. Mackenzie, on "The Influence of Pure Science on Progress." The Day and Evening courses of study, comprise the various branches of Natural Science, Mathematics, Classical and modern Languages, Economics, Commercial Subjects, Law, Mental Science, and Art. The courses provide for the Examinations of the University of London, in the faculties of Arts, Science, and Commerce, and also for those of the Conjoint Board, Civil Service, &c. The Report for the last session shows that during the year 71 students passed some University examination, while large numbers gained successes at other public examinations. The College has had many additions to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are very highly equipped. The Day classes provide courses in Chemistry, Zoology, Botany, Physics, Mathematics, and Geology for the Science Degrees of London University, and a complete course of instruction in Metallurgy and Mining. There are also Day classes in Latin, Greek, and modern Languages. The School of Art is open both day and evening. The Metallurgical laboratory has been extended and reorganised, and classes are held both in the day and evening. The Calendar supplies complete syllabuses of the classes and full information about the College. A Lecture or Entertainment is given in the Theatre every Wednesday evening.

BRITTON SCHOOL OF CHEMISTRY AND PHARMACY, 171, Brixton Road, London.—Principal, Dr. A. B. Griffiths, F.R.S. (Ed.). Lectures on Inorganic and Organic Chemistry, Physics, Botany, &c., for Pharmaceutical, Medical, and other students. The benches in the laboratory are fitted with every convenience. There are courses in Research Work. Full particulars as to fees, &c., may be obtained by writing to the Principal.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road (near the Obelisk).—Chemistry: Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry (Session fees, per course, 10s. to 20s.). Day Practical class in Electro-chemistry, lecture on Friday evenings. Special Saturday Morning Class in Practical Chemistry (10s.); Dr. F. Mollwo Perkin, assisted by H. B. Law, B.Sc., and A. J. Hale. Electricity and Magnetism: Evening Lectures and Laboratory Work (Session fees, per course, 10s.), Dr. J. Henderson, assisted by H. Saunders. Special Evening Courses on Painter's Oils, Colours, and Varnishes. Session opens Monday, October 3, 1904.

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, &c. Systematic Courses are held for the Matriculation, Intermediate Science, and B.Sc. Examinations of the University of London. Prospectuses of Day and Evening Classes may be obtained from the Secretary, 1d. each, by post 3d. each.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Lectures and Practical Classes in General Chemistry and Photography, also in Chemistry applied to other industries, are held in the evenings from 7.15 to 10, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties. Session commences September 21.

EAST LONDON TECHNICAL COLLEGE, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Assistants, Clarence Smith, D.Sc., and F. G. Pope. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to work for the Honours Examination and research. Evening Classes

for London University Degrees are also held. The Day College opens on Sept. 19. Evening Classes begin Sept. 26.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

IMPERIAL COLLEGE OF CHEMISTRY AND PHARMACY, 49 and 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *re* the Institute of Chemistry Examination. Students attending the College visit technical works.

CARPENTERS' COMPANY TECHNICAL INSTITUTE, Jupp Road, Stratford, E.—Principal, William Ping, F.C.S. Evening Classes in Theoretical and Practical Chemistry, and in many other Departments of Science and Art. Day Technical School. Session begins September 19.

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Principal, Charles A. Kohn, M.Sc., Ph.D., &c., assisted by R. S. Willows, D.Sc., and C. O. Bannister, A.R.S.M. Evening Classes in Chemistry, Metallurgy, Physics, and Mathematics, designed to meet the requirements of those engaged in Chemical, Metallurgical, and Electrical industries, and also in other departments of Science and Art. Practical laboratory work. Classes begin September 26. Full details may be obtained on application, or by letter to the Principal.

THE POLYTECHNIC, 309, Regent Street, W.—University of London Preparation Classes. Session begins Sept. 16.

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, (i.) to promote the better education of persons desirous of becoming public and technical analysts and chemical advisers on scientific subjects; (ii.) to examine Candidates, and to grant certificates of competency; and (iii.) to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship*.—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University approved by the Council, or in the laboratory of a Fellow of the Institute, with the object of adopting the profession of Analytical and Consulting Chemistry. *The Intermediate Examination*.—Candidates for admission to the Intermediate Examination are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Advanced Mathematics; (ii.) Mechanics and Chemical Engineering; (iii.) Metallurgy; (iv.) Geology and Mineralogy; (v.) Physiology; (vi.) Bacteriology; and (II.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' training in a recognised Institution as indicated above, and work systematically for two other years in the laboratory of a Fellow of the Institute. A Candidate who has taken a Degree in Science (including

Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also passed in at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship (A.I.C.)*.—Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship (F.I.C.)*.—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of Applied Chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained on application to Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C. Price One Shilling.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Mr. Robert H. Pickard, D.Sc. (Lond.), &c., assisted by Mr. Jos. Yates and Mr. Allen Neville, B.Sc. (Lond.), F.I.C. Session opens Monday, September 12. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 2½d.).

COUNTY TECHNICAL LABORATORIES, Chelmsford.—The new buildings are now open, and comprise facilities for practical instruction in Chemistry and Biology in their relation to Agriculture. Lecturer in Agricultural Chemistry, T. S. Dymond, F.I.C.; Assistants, G. Clarke, A.I.C., and others. Prospectus free on application.

REDRUTH SCHOOL OF MINES, CORNWALL.—Principal, Howard C. Ridding, A.R.S.M., F.I.C., assisted by a staff of Mining Engineers and Mine Surveyors. Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, and Blowpipe Analysis, for intending Assayers and Mineral Chemists. Shorter Courses are also held in the above subjects to meet the requirements of intending Mining Engineers, and Prospectors. Practical instruction in Mining given at Pednandrea, the School Mine. Syllabus on application to the Registrar. Session commences Wednesday, September 7.

LEEDS INSTITUTE: TECHNICAL SCHOOL, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in 41 subjects of Science and Technology, among which are:—Chemistry, Inorganic and Organic, Theoretical and Practical, by Mr. R. E. Barnett, B.Sc.; A.R.C.S.; Mr. J. B. Murray, Mr. A. McFarlane, and Mr. F. R. Penn; Metallurgy, Theoretical and Practical, and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Magnetism and Electricity, and Practical Physics, by Mr. J. E. Tindall, B.A., B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker; Photography, by Mr. S. E. Bottomley. Fees:—Lectures, from 5s. 6d. per Session; Laboratory work, from 5s. 6d. Systematic courses arranged for Pharmaceutical Students and for those engaged in Chemical Industries at composition fees. Session commences Sept. 19th. Prospectuses of various Classes free on application to the Secretary, Mr. Arthur Tait. Calendar of the Institute (218 pp.) post free 5d.

THE MUNICIPAL SCHOOL OF TECHNOLOGY, Sackville Street, Manchester.—This fine building occupies an area of upwards of 6800 square yards, and is six floors in height. Its equipment, which is nearly complete, is on a scale of great magnitude. It comprises laboratories and workshops for Mechanical, Electrical, and Hydraulic Engineering, for the Textile industries, for Photography, Collotype and Photo-mechanical processes, for the Letterpress and Lithographic industries, and for the industries included

within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises, in addition to ample accommodation for pure Chemistry, laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity.

WOLVERHAMPTON MUNICIPAL SCIENCE AND TECHNICAL SCHOOL.—Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Messrs. W. Whitehouse and A. T. Harrison, B.Sc.; Botany, Mr. Sidney Phillips, Ph.D. Day Classes in Chemistry and Physics, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. Session commences Monday, Sept. 12th. For other particulars and programme, apply Mr. G. F. Chell, Registrar.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1904, the Chemical Laboratory Fresenius was attended by thirty-six Students. Of these twenty-nine were from Germany, two from England, and one from Austria, Luxemburg, France, Italy, and Russia. There were three Assistants in the Instruction Laboratory, and twenty-five in the Versuchsstationen (private laboratories). To the teaching staff of the Institution belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Prof. Dr. Med. G. Frank, Dr. L. Grünhut, Dr. E. F. Grosse, and Architect J. Huber. The next Winter Term begins on October 17. In the Summer Term, 1904, besides scientific work, there were many examinations carried on in the different departments of the Laboratory (Versuchsstationen) in the interests of trade, industry, mining, agriculture, hygiene, justice, and government.

EAST LONDON TECHNICAL COLLEGE, MILE END ROAD, E.

Session 1904-1905 commencing September 19 1904

DAY AND EVENING COURSES for the B.Sc. (Honours and Pass) Degree of the University of London are conducted by the following Lecturers, who are recognised teachers of the University of London:—

Mathematics	J. L. S. HATTON, M.A., and
Physics	W. F. S. CHURCHILL, M.A.
Chemistry	R. A. LEHFELDT, D.Sc., &c.
Botany	J. T. HEWITT, D.Sc., Ph.D., and
Engineering	C. SMITH, D.Sc.
Electrical Engineering	V. H. BLACKMAN, M.A.
	D. A. LOW, M.I.M.E.
	J. T. MORRIS.

The Day Courses in **ENGINEERING and CHEMISTRY** are also suitable for those entering manufacturing firms.
Calendar 2d. post free on application.

J. L. S. HATTON, Director of Studies.

THE MUNICIPAL SCHOOL OF TECHNOLOGY, SACKVILLE STREET, MANCHESTER.

THE ENTRANCE EXAMINATIONS for the Day Departments in—

MECHANICAL, ELECTRICAL, and SANITARY ENGINEERING.

The **CHEMICAL INDUSTRIES**, including BLEACHING, DYEING, PRINTING, PAPER-MAKING, BREWING, METALLURGY;

ARCHITECTURE and BUILDING CONSTRUCTION;

The **TEXTILE INDUSTRIES**;

PHOTOGRAPHY and PRINTING;

will be held on **MONDAY, TUESDAY, and WEDNESDAY, SEPTEMBER 12, 13, and 14, at 9.15 a.m.** Prospectus and entrance forms on application.

The **SCHOOL RE-OPENS on MONDAY, SEPTEMBER 19, at 9.15 a.m.**

J. H. REYNOLDS, Principal.

GRIFFIN'S METALLURGICAL BOOKS.

An Introduction to the Study of Metallurgy.

By SIR W. ROBERTS-AUSTEN. FIFTH EDITION. 18s.

The Metallurgy of Gold. By T. KIRKE ROSE. FOURTH EDITION. 21s.

The Metallurgy of Lead and Silver. By H. F. COLLINS. VOL. I.—LEAD. Price 16s. VOL. II.—SILVER. Price 16s.

The Metallurgy of Iron. By THOMAS TURNER. SECOND EDITION. 16s.

The Metallurgy of Steel. By F. W. HARBORD. With Section on Mill Practice, by J. W. HALL. 25s. net.

METALLURGICAL ANALYSIS and ASSAYING, for STUDENTS. By W. A. MACLEOD and C. WALKER. 12s. 6d. net.

ASSAYING. By J. J. BERINGER and C. BERINGER. NINTH EDITION. 10s. 6d.

ELECTRIC SMELTING and REFINING. By Dr. W. BORNHORS and W. G. McMILLAN. SECOND EDITION. 25s. net.

ELECTRO-METALLURGY. By W. G. McMILLAN. SECOND EDITION. 10s. 6d.

CYANIDING GOLD and SILVER ORES. By H. FORBES JULIAN and EDGAR SMART. 21s. net.

THE CYANIDE PROCESS of GOLD EXTRACTION. By JAMES PARK. THIRD ENGLISH EDITION. 7s. 6d.

ELEMENTARY METALLURGY. By A. HUMBOLDT SEXTON. THIRD EDITION. 6s.

LECTURES on IRON FOUNDING. By THOMAS TURNER. 3s. 6d. net.

GRIFFIN'S TECHNOLOGICAL BOOKS.

Gas Manufacture. By W. J. A. BUTTERFIELD. THIRD EDITION, thoroughly Revised. Vol. 1. 7s. 6d. net.

Acetylene. By F. H. LEEDS and W. J. A. BUTTERFIELD. 5s. net.

Oils, Fats, and Waxes. By C. R. ALDER WRIGHT and C. A. MITCHELL. SECOND EDITION. 25s. net.

Lubrication and Lubricants. By L. ARCHBUTT and R. M. DEERY. Illustrated. 21s.

The Chemistry of Indiarubber. By Dr. CARL O. WEBER. 16s. net.

Painters' Colours, Oils, and Varnish. By GEORGE H. HURST. THIRD EDITION, Revised. 12s. 6d.

Painters' Laboratory Guide. By G. H. HURST. 5s.

TRADES' WASTE: Its Treatment and Utilisation. By W. NAYLOR. 21s. net.

SEWAGE DISPOSAL WORKS. By W. SANTO CRIMP. SECOND EDITION. 30s.

WATER SUPPLY: Its Sources and Selection. By R. MIDDLETON. 8s. 6d. net.

SANITARY ENGINEERING. By FRANCIS WOOD. 8s. 6d. net.

ROAD MAKING and MAINTENANCE. By THOS. AITKEN. 21s.

GRIFFIN'S CHEMICAL BOOKS.

A Short Manual of Inorganic Chemistry. By A. DUPRÉ and WILSON HARR. THIRD EDITION. 6s. net.

Quantitative Analysis. By A. HUMBOLDT SEXTON. FOURTH EDITION. 3s.

Qualitative Analysis. By A. HUMBOLDT SEXTON. FOURTH EDITION. 3s. 6d.

Foods: Their Composition and Analysis. By A. and M. WYNTER BLYTH. FIFTH EDITION. 21s.

Poisons: Their Effects and Detection. By A. WYNTER BLYTH. THIRD EDITION. 21s.

Dairy Chemistry. By H. DROOP RICHMOND. 16s.

Milk: Its Production and Uses. By EDWARD F. WILLOUGHBY. 6s. net.

Flesh Foods. By C. A. MITCHELL. 10s. 6d.

FIRE and EXPLOSION RISKS. By Dr. VON SCHWARTZ. Translated by C. T. C. SALTER. 16s. net.

CHARLES GRIFFIN AND COMPANY, LTD.
Exeter Street, Strand, London.

THE SIR JOHN CASS TECHNICAL INSTITUTE. JEWRY STREET, ALDGATE, E.C.

Principal—CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.

EVENING CLASSES IN CHEMISTRY, METALLURGY, PHYSICS, and MATHEMATICS.

Designed to meet the requirements of those engaged in CHEMICAL, METALLURGICAL, and ELECTRICAL INDUSTRIES, and in trades associated therewith.

Also preparation for the B.Sc. Examination of London University. Every facility for Special and Advanced Practical Work in well-equipped Laboratories, both in the Afternoon and Evening

CHEMISTRY { CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.
PHYSICS { R. S. WILLOWS, D.Sc., M.A.
METALLURGY { C. O. BANNISTER, Assoc. R.S.M.
MATHEMATICS { G. M. K. LEGGETT, B.A.

CLASSES IN METALLURGY.

GENERAL METALLURGY.
THE METALLURGY OF GOLD, SILVER, and LEAD.
FUEL and REFRACTORY MATERIALS.
METALLOGRAPHY, including PYROMETRIC WORK.
ASSAYING.

ANALYTICAL CHEMISTRY,

Including ELECTROLYTIC and GAS ANALYSIS.

Each Course of Lectures will be accompanied by suitable Laboratory Work.

GLASS BLOWING.

A series of Courses of Instruction will be given during the Session by Mr. A. C. COSSOR.

New SESSION begins MONDAY, SEPT. 26th.

The Institute is readily accessible, and near to Fenchurch Street, Liverpool Street, Broad Street, and Metropolitan Railway Stations. For details of the Classes apply at the Office of the Institute, or by letter to the PRINCIPAL.

W. H. DAVISON, M.A.,
Clerk to the Governing Body.

THE POLYTECHNIC, 309, REGENT STREET, W.

UNIVERSITY OF LONDON PREPARATION CLASSES.

Full Courses of Instruction for Matriculation, Inter. Arts, Science, and Engineering, and Final Arts. Special Courses for Final B.Sc. in Mathematics, Physics, and Chemistry.

Examinations are held at the above Institute.

NEXT TERM commences SEPTEMBER 16th, 1904.

Courses are so arranged that Students can do the work on Saturday and one evening per week.

Full particulars can be obtained on application to the DIRECTOR OF EDUCATION

CITY OF LONDON COLLEGE,

WHITE STREET and ROPEMAKER STREET,
MOORFIELDS, E.C.

MICHAELMAS TERM commences OCTOBER 3rd.

CLASSES and LABORATORY WORK in CHEMISTRY, PHYSICS, BIOLOGY, BOTANY, GEOLOGY, and PHYSIOLOGY. Special preparation for the Examinations of the Pharmaceutical Society, The Conjoint Board. Complete Courses for University Matriculation and Inter. and Final B.Sc., meeting during the Evening and on Saturdays.

Full particulars gratis on application to—

DAVID SAVAGE, Secretary.

REDRUTH SCHOOL OF MINES, CORNWALL.

Session 1904-1905 begins September 7th.

A "Mining Certificate" is awarded to Students passing successfully through the School Course.

PRACTICAL MINING CLASSES, under the Instruction of Capt. WILLIAM HAMBLEY (late Government Inspector, South Africa). Distinctions in Mine Surveying in Open Examination five years in succession, including five Medals and Prizes, being all the awards of the City and Guilds of London Institute in 1904 in this subject.

SYLLABUS and every information on application to—

THE REGISTRAR.



RADIUM BROM.

POLONIUM.

RADIO-ACTIVE ORES.

BAR.-PLAT. CYAN. SCREENS.

" LARGE CRYSTALS.

ETC., ETC.,

ALL AT REASONABLE PRICES.

Armbrecht, Nelson & Co.,

71-73, Duke-st., Grosvenor-sq., W.

*Phone—4942 Gerard.

BIRKBECK COLLEGE,

Breams Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

CHEMISTRY J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS A. GRIFFITHS, D.Sc.
MATHEMATICS E. H. SMART, M.A.
BOTANY A. B. RENDLE, M.A., D.Sc.
ZOOLOGY H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING .. G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board, Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.

CARPENTERS' COMPANY'S

TECHNICAL INSTITUTE, JUPP ROAD, STRATFORD, E.

CLASSES

IN

SCIENCE, ART, TECHNOLOGY, and LANGUAGES.

Chemical and Physical Laboratories.

Manual Training.

Workshops for PLUMBING, ENGINEERING, CARPENTRY and JOINERY, &c., WOOD-CARVING.

OPENS on MONDAY, SEPTEMBER 19th.

Prospectus on application.

THE CHEMICAL NEWS

VOL. XC., No. 2338.

A SUGGESTED EXPLANATION OF THE PHENOMENA OF OPALESCENCE OBSERVED IN THE NEIGHBOURHOOD OF CRITICAL STATES.*

By F. G. DONNAN.

It has been frequently observed (Guthrie, Rothmund, Friedländer, Konowalow) that a mixture of two liquids becomes opalescent before the temperature is reached at which definite separation into two phases occurs. Similarly a mixture of two partially miscible liquids remains opalescent at temperatures beyond that corresponding to the disappearance of the meniscus. Apparently analogous phenomena have been noticed in the case of one-component liquid-vapour systems, especially by Wesendonck and Teichner. The latter has observed the existence of permanent opalescent states in the case of carbon tetrachloride at temperatures several degrees higher than the critical. These phenomena, so far as they refer to mixtures of liquids, have been studied by Konowalow, who considers that they are due to a partial separation into two phases, occurring round dust-nuclei acting as centres of disturbance. Konowalow shows that such a disturbance of equilibrium in the otherwise homogeneous liquid will, in the neighbourhood of the critical solution temperature, involve only a slight expenditure of work owing to the small change of vapour-pressure with composition under these conditions.

The author suggests another explanation which involves the following suppositions:—

(a) Below the critical temperature the interfacial tension between the two phases is positive for all values of the radius of curvature.

(b) At the critical temperature the interfacial tension becomes zero for all ordinary curvatures, but remains positive for very small values of the radius of curvature. It will be seen that this assumption involves the further one, that at the temperature of disappearance of the meniscus at a bounding surface of ordinary curvature (critical temperature) the two phases do not become identical.

(c) At temperatures slightly above the critical the interfacial tension is still positive for very small radii of curvature, but negative for all ordinary curvatures.

(d) At still higher temperatures the interfacial tension becomes negative for all curvatures.

These assumptions carry with them the main assumption that the interfacial tension between two liquid phases increases in general with diminution of the radius of curvature of the bounding surface. This increase, however, need not extend to the very smallest values of the radius of curvature. It is also necessary to suppose that the curve connecting interfacial tension with radius of curvature of the bounding interface suffers a shift towards the region of negative values of the interfacial tension as the temperature rises.

Granting these assumptions, the existence of permanent opalescent states above the ordinary critical-point follows at once. For it can be shown that the conditions specified, for example, under (c) would produce a system in which one phase would be distributed throughout the other in a state of very fine sub-division. If the particles are small enough such a system would not present a milky appearance, but would doubtless be opalescent.

An interesting question concerning the nature of the critical state is thus raised, namely, as to whether there is not sufficient experimental evidence to justify the belief that the passage of systems through critical states is in-

adequately described by the simple theory of Andrews? That is the wider question at issue. The particular form of explanation suggested in the present paper also raises the question as to whether the observed phenomena may not admit of interpretation by taking into consideration the operation of capillary forces?

These points seem worthy of discussion, especially in relation to the theories of "gaseous" and "liquid" molecules, "Gasonen" and "Fluidonen" devised in recent years by de Heen, Traube, and others.

The present communication has arisen out of a correspondence on the subject with Professor van't Hoff, to whom the main idea is due.

ON THE ENERGY OF WATER AND STEAM AT HIGH TEMPERATURES.*

By Professor C. DIETERICI.

THE author has devised a method for determining the specific heat of water at temperatures up to 300° C. The water is inclosed in quartz tubes, which are sufficiently strong to withstand the pressure of steam—namely, about 100 atmospheres at 300° C.—and the determinations are made with the aid of the ice calorimeter. The results obtained may be expressed by the formula—

$$c_1 = 1.0160 - 0.006057 t + 0.004302 t^2;$$

in which the specific heat, c_1 , is given as a function of the temperature. The formula holds between 50° and 300° C., but does not hold below 50° C., because at such low temperatures the point of maximum specific heat first observed by Rowland occurs.

The observations made with water completely enclosed in a tube give the difference between the energy of the liquid water at t° C. and that of the water at 0° C. Since the heat of evaporation is known or calculable, this quantity, diminished by the external work, gives the energy difference between saturated steam and liquid water at t° C.

Very careful observations have been published by Sir W. Ramsay and S. Young (*Phil. Trans.*, 1891) on the pressure of unsaturated steam between 140° and 270°; and since the relation between energy change and volume at constant temperature is given by the equation—

$$\left(\frac{\partial U}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p,$$

of the mechanical theory of heat, the change of energy of superheated steam depends only on the pressure, and can be calculated from the author's present observations. It is therefore possible to calculate the energy isothermals and to draw the isothermal lines for water.

After applying the most accurate methods of calculation possible to the new observations, the author draws the following conclusions:—

At about 200° C. the specific heat of superheated steam at constant volume is 0.5° , and is practically independent of the volume if the latter is much greater than the saturation volume. As, however, the volume diminishes to the volume of saturation, the specific heat increases to about 0.7° . The specific heat at constant pressure, C_p , similarly varies from 0.6 to 0.8 . Further, in the well-known equation of state of van der Waals,—

$$p + \pi = \frac{RT}{v - b},$$

the cohesion pressure, π , cannot be taken as $\frac{a}{v^2}$, but is such a function of v and T that it has a considerable value for large volumes at low temperatures, and for small volumes at high temperatures.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

ON DOUBLE ACETYLIDES.*

PART I.

By Major A. E. EDWARDS and Prof. W. R. HODGKINSON.

The authors have investigated the action of acetylene on a number of salts with a view to obtaining an explosive of a sufficiently safe nature to be used for military purposes, and refer in the present paper to some silver compounds which they have obtained. The acetylene employed was purified as well as possible from sulphur and phosphorus compounds, and was then brought in contact with silver salts in solution or suspended in boiling water. In some cases the gas was passed for some days continuously through the water containing the suspended salts.

A number of organic salts, such as silver acetate, benzoate, and butyrate, yield the same acetylide as that obtained from neutral or faintly alkaline silver nitrate solution. A solution of silver nitrate in nitric acid of 1·3 sp. gr. did not give this particular acetylide, but one containing nitric acid as nitrate. Solutions of silver salts in potassium cyanide or in thiosulphate are quite unaffected by acetylene, but pure thiocyanate suspended in water is acted upon; the product in this case is explosive, and contains both sulphur and cyanogen, but was not obtained in a pure state.

The following compounds have been obtained in a definite form, analysed and examined as to their sensitiveness to percussion and heat.

From a boiling solution of silver bichromate acetylene precipitates an orange-red salt of the composition $(Ag_2O \cdot 2H_2O \cdot Ag_2CrO_4)$, whilst chromic acid is liberated. When dry this substance is very sensitive to friction, and explodes violently at 157° C. Corresponding compounds are formed from silver sulphate, selenate, tungstate, and molybdate; they are all much less sensitive than the chromic acid compound, and explode much more feebly.

Compounds from the phosphate and vanadate were obtained with difficulty, and no satisfactory analyses were made; they explode in a very feeble but peculiar manner.

ON THE CHARACTERISTIC SULPHUR LINES
IN THE PHOTOGRAPHIC SPECTROSCOPY
OF MINERALS.*

By M. le Comte A. DE GRAMONT, D.Sc.

In previous papers† I have given the descriptions and measurements that have been obtained by direct observation in the visible portion of the spectrum of the electric spark striking between two fragments of minerals connected respectively to the two poles of an induction coil through a condenser. Under these conditions the spark shows, not only the metallic lines, but also those of the *metalloids* which are present in combination in the mineral. Fused salts have also given me the same results, which may be summed up as follows:—

The condensed spark, striking on the surface of a compound, dissociates it, giving a very bright line spectrum, in which each substance—metal or metalloid—is represented by the characteristic lines of its own spectrum. Thus we have a decomposition spectrum, or true "spectrum of dissociation," which may be looked upon simply as formed by the superposition of the spectra of the elements present in the compound.

I have followed up this examination with photographic methods. The results obtained now only apply to a portion of the visible lines; that is to say, from a small part of

the green to the extreme violet, and thence to the whole of the ultra-violet. The characteristic lines of the elements are thus no longer the same, at least to a great extent, and I propose here to describe those of sulphur.

I have made use of coils the powers of which varied from 3 c.m. sparks up to sparks of 20 c.m. in length, and of condensers consisting of Leyden jars each having 12 square decimetres of surface, which corresponds to a capacity of 0·043 microfarad; I used as many as six jars with the large coil. A variable spark gap was introduced into the secondary circuit, so as to regulate the frequency and the potential of the spark without altering the distance apart of the fragments of mineral, which were kept at about 1 m.m. at the most, fixed in platinum forceps similar to those used with the blowpipe. It was also possible to introduce into the same circuit self-inductors of different sizes; these have enabled me to eliminate the air spectrum (with two jars and a self inductor of 0·00008) without diminishing the intensity of the sulphur lines to any great extent, which disappear, however, with a self-inductor of slightly larger size. After having suppressed the air spectrum, we are able to reinforce that of the sulphur by increasing the condensation by adding another jar (*Comptes Rendus*, May 5, 1902).

The most easily recognisable sulphur lines are in the green:— α (5665 to 5599), β (5473 to 5429), γ (5243 to 5320), δ (5213 to 5201). These are the most sensitive for chemical research, but it has been found also that the portion of the spectrum which acts on ordinary photographic plates—the most characteristic sulphur lines for photographic purposes—is the following, all the lines being of considerable intensity:—

$S\eta$	4812·0	
$S\theta$	4716·4	
	4552·6	
$S\mu$	4525·1	
	4483·6	
	4464·2	
	4362·6	
	4354·7	
	4332·9	
	4294·6	
$S\pi$	4285·1	
	4267·2	
	4253·8	
		$S\rho$ {
		4189·9
		4174·5
		4162·9
		4153·3
		4145·3
		4142·4
		3933·6
		3919·5
		3495·4

Double.

This spectrum was obtained with a spark between two fragments of galena (PbS) and argyrose (Ag_2S). Above the spectrum of the mineral was placed, on the same plate, the spectrum of sulphur obtained from a Plücker tube heated and filled with the vapour of this metalloid, and of which the lines are extended into the two spectra. The spectrograph consisted of two prisms of heavy flint glass and an achromatic objective of 33 c.m. focal distance. The wave-lengths of the sulphur lines given here are taken from the paper by MM. Eder and Valenta ("Die Spectren des Schwefels," *Denkschriften des Kais. Akad. d. Wissenschaften*, lxvii., Wien, 1898) obtained with a scale; my measurements, compared with the lead and silver lines, agreed with those of MM. Eder and Valenta, to about two units in the fifth figure.

On the other hand, the relative intensities of the ultra-violet lines were different from those observed by these authors, and I feel compelled to give here three principal lines I found in this part of the spectrum, which I examined with a spectrograph with quartz prism and lenses. Further, the important lines, from the analytical point of view, are those of the group $S\mu$, $S\pi$, and especially $S\rho$; they can be obtained, as is seen, with flint prisms, which makes their detection more simple for chemists, and enables a greater dispersion to be reached, thereby separating the different groups of lines.

I propose to continue the study of the sulphur lines in the most refrangible portion of the ultra-violet spectra, using the fused alkaline sulphates.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

† *Comptes Rendus*, July 2, 1894, and July 8, 1895; *Bull. Soc. Française de Minéralogie*, 1895; "Analyse spectrale directe des minéraux," vol. i., 1895; and *Bull. Soc. Chim. de Paris*, Series 3, vol. xiii.

NEW LOW TEMPERATURE PHENOMENA AND THEIR SCIENTIFIC APPLICATIONS.*

By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S.

THE matter the author was about to bring before the Section, speaking generally, was not exactly new as it related to the absorption of gases by charcoal. It was found by Saussure about the beginning of last century that gases were absorbed by charcoal to a variable extent, and, moreover, that some kinds of charcoal were more active than others. Coconut charcoal, Hunter discovered about 1865, possessed twice the condensing power of any previously prepared charcoal. Very little, however, had been done in this field of investigation for years, but with the advent of Crookes's radiometer and Sprengel's vacuum pump the application of charcoal for removing gases from the residual vacuum was tried by Tait and the author about 1875. It was easy to solidify all traces of condensable gases, such as carbonic anhydride, sulphur dioxide, &c., out of any vessel by the use of liquid air, and even the less condensable gases could be removed from any space by a similar application of liquid hydrogen.

Wishing to investigate thermal interactions at low temperatures the author had made an attempt to induce palladium and hydrogen to combine under such conditions, but the result was a failure. He then resorted to the use of coconut charcoal, and the results obtained the author had recently described in two papers communicated to the Royal Society, respectively entitled "The Absorption and Thermal Evolution of Gases Occluded in Charcoal at Low Temperatures" and "The Separation of the Most Volatile Gases from Air without Liquefaction" (see CHEM. NEWS, vol. xc., pp. 73 and 90). Demonstrating the absorptive properties of this substance, he first showed that some charcoal contained in a tube when immersed in liquid air absorbed air with great avidity; if the supply was cut off a very high vacuum at once ensued.

In another experiment air at atmospheric pressure in a Crookes's radiometer was placed in connection with a tube containing charcoal. The radiometer vanes remained absolutely still when placed in the beam of light from the electric lamp, but shortly after the charcoal was immersed in liquid air the vanes began to move, and soon attained a great velocity, indicating a very high vacuum. When the liquid air was removed, the radiometer soon slackened, and gradually but rapidly came to rest again, showing that the air resistance had been restored in the radiometer, and that the gas absorbed by charcoal at a low temperature was given off again when the temperature was raised. When a current of air was passed over charcoal saturated with air at $-185^{\circ}\text{C}.$, the escaping gas was at first all nitrogen, and in a quarter of an hour the gas held by the charcoal contained as much as 58 per cent of oxygen, instead of the usual 21 per cent. By simply raising the temperature this 60 per cent air could be collected, but if the air was taken off in two successive portions the percentage of oxygen rose to nearly 80 per cent in the last half. All gases were absorbed in larger quantities at $-185^{\circ}\text{C}.$ than at $0^{\circ}\text{C}.$; helium was absorbed in smallest quantity, and then followed neon, hydrogen, nitrogen, argon, carbonic oxide, and oxygen, but with gaseous mixtures the absorption was still greater.

The lecturer then showed by a series of beautiful vacuum tube experiments the behaviour of nitrogen, oxygen, hydrogen, and argon when submitted in contact with charcoal to the cooling influence of liquid air. A nitrogen tube, for instance, exhibited the usual violet colour when the spark passed through it, but as soon as the charcoal was immersed in the liquid air the tube passed through various stages of attenuated brilliancy until ultimately the vacuum became so high that the current could scarcely overcome the resistance. When the liquid air was removed

the changes were passed through in the reverse order. Oxygen passed through a similar series of changes, but in the case of hydrogen the absorptive power of the charcoal at the temperature of liquid air was not great enough to render the tube non-conductive. In the case of argon the light due to that element rapidly disappeared with the cooling of the charcoal, but a brilliancy remained due to a considerable residue of helium and neon, which was not absorbed. Nitrogen from air did not exhibit this character to the same extent, because the quantity of helium and neon was 100 times less than in the argon. It is possible by means of charcoal absorption and by the use of different condensation temperatures to separate gases from mixtures and to examine various gases spectroscopically. For instance, in the unabsorbed residue from 200 c.c. of air, neon and helium can be detected by the spectroscope after the nitrogen and oxygen are absorbed, and the brilliant ruddy glow of the neon discharge is most brilliant in the residue from three litres of air. By boiling out 300 c.c. of gas from sea-water, rain-water, Cambridge water, and London water, and subjecting it to fractionation by means of charcoal absorption at low temperature, helium and neon had been detected in all cases, showing that these elements were more extensively disseminated than was previously supposed.

Finally, the author said that hydrogen could be completely absorbed by charcoal at the boiling-point of hydrogen, and that helium at the temperature of solid hydrogen, 15° absolute, was similarly condensed. It resulted from these experiments that the helium boiling-point would be about 5° or 6° absolute, so that Lord Kelvin's predicted 5° absolute might yet be obtained.

THE RELATION BETWEEN THE CRYSTALLINE AND THE AMORPHOUS STATES AS DISCLOSED BY THE SURFACE FLOW OF SOLIDS.*

By G. T. BEILBY.

IN former papers the phenomena observed in connection with the flow of solids have been fully described, and in the most recent of these the results of the observations have been applied to the study of the hard and soft states in metals. The purpose of the present paper is to direct attention to the very general character of the relations which have been found to exist between the amorphous and the crystalline states.

Observations on flow in crystalline substances are described and illustrated by photo-micrographs. By the use of etching in stages the successive layers of a polished or disturbed surface are disclosed, from the smooth vitreous surface, through a granular layer to the undisturbed crystalline body beneath. The demonstration that the polish of a lens of rock crystal has resulted from the formation of a flowed layer of amorphous phase on its surface suggests that no crystalline substance is too hard to yield to the mechanical flowing action.

The passage of the amorphous back to the crystalline state by the agency of heat is discussed, and attention is directed to the important bearing of the fact that this transformation occurs at a definite temperature, on the behaviour of solids at ordinary atmospheric temperatures. It is suggested that as the stability-point of ice is probably a long way below the freezing-point, the amorphous phase can only have a transient existence at ordinary atmospheric temperatures; while at the lower range of winter temperatures within the Arctic Circle, the amorphous phase, once formed, may be stable and permanent.

The grinding of crystalline substances to powder does not simply consist in their reduction to finer and finer

* Abstract of a Lecture delivered before the British Association (Section B), Cambridge Meeting, 1904.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

crystalline fragments, but it involves the transformation of at any rate a part of the substance into the amorphous condition.

When crystalline powders are formed into cakes by pressure the cementing material is the amorphous phase which results from flow.

In metals, and probably in most other solids, the physical and other properties of the two phases are so distinct that it is not difficult to determine the transition temperature or stability-point in the transformation $A \rightarrow C$.

From the existence of a definite stability-point it is argued that not only must all crystalline substances be capable of existing in the amorphous as well as in the crystalline state, but that, by purely mechanical means, it is possible to transform them into this state.

These observations, and the conclusions to which they have led, have a very direct bearing on the flow of rocks. The recognition of the transformation from crystalline to amorphous through an intermediate mobile phase, for the first time supplies an explanation of why flow which has been started by stresses can cease while the disturbing stresses are still maintained.

ON SOME REACTIONS BETWEEN AMMONIUM SALTS AND METALS.*

By W. R. HODKINSON and ARTHUR H. COOTE.

As far back as 1879, a note was published by one of us on the action of aluminium on ammonium chloride, and we have recently continued the investigations of the behaviour of ammonium salts generally towards metals.

Ammonium nitrate, either in aqueous solution or in a fused state, acts very vigorously on some metals.

There is a notable difference, as a rule, between the fused salt and its aqueous solution in regard to rate of action on the more common metals; but in the case of the metal cadmium there is little difference perceptible between the rate of action of an aqueous solution and the melted salt. Cadmium placed in an ice-cold saturated solution of ammonium nitrate rapidly dissolves without evolution of gas. The liquid becomes alkaline from presence of a little free ammonia; the solution gives off nitrogen only when heated to 100° , when the cadmium ceases to dissolve and some remains in excess. The solution contains a little free ammonia, and apparently the nitrite of cadmium and ammonium. This is, at any rate, indicated by the fact that every trace of cadmium can be precipitated from this solution by passing through it a stream of carbon dioxide at the ordinary temperature. The solution contains mainly ammonium nitrite.

Zinc and magnesium act in a similar manner, but, owing to the formation of somewhat insoluble double ammonium compounds, not to the same extent or with the rapidity observed with cadmium. Aluminium, iron, mercury, and silver are unaffected by an aqueous solution of the salt, but nickel, copper, and lead are slightly active. Lead becomes coated with a somewhat insoluble nitrite.

Melted ammonium nitrite has no action on iron, mercury, or aluminium, and, in fact, these metals are quite unaffected when the salt is heated with them so strongly as to decompose with formation of red fumes; under these conditions silver is slightly attacked. Approximately it may be stated that when the salt is just fused the following metals are acted upon at rates about in the order given:—Cadmium, magnesium, zinc, copper, nickel, lead, bismuth.

The mechanism of the reaction as regards cadmium and fused ammonium nitrate seems to be that first a little ammonia is split off, and then a metallic nitrate formed. This, however, involves the expulsion of hydrogen, which in turn reduces the nitrate of the metal to nitrite, which

immediately reacts with the ammonium salt in the usual manner, liberating nitrogen.

Weighed quantities of metals have been allowed to act upon ammonium nitrate in a vacuum-tube maintained at the melting-point of the salt. In the cases of cadmium and copper the gas collected was pure nitrogen; with cadmium the amount of nitrogen collected falls a little short of 4 atoms of nitrogen to 1 atom of metal; with copper it is nearly 3 atoms of nitrogen to 2 atoms of the metal. The amount of ammonia liberated in the first phase of the reaction may have something to do with this deficit of nitrogen, but we are unable to explain it fully at present.

Powdered cadmium dissolves in a solution of aniline nitrate, and if the temperature be maintained below 10° no appreciable evolution of gas occurs, and a considerable yield of diazoaminobenzene is obtained. The course of the reaction is very similar to that with the ammonium salt, a little aniline being liberated in the first instance.

ON CRYSTAL STRUCTURE AND ITS RELATION TO CHEMICAL CONSTITUTION.*

By Prof. PAUL GROTH.

THE molecular hypothesis assumes that in solid bodies the molecular movements occur about certain equilibrium positions which can only be altered by the operation of external forces. In crystalline bodies the spacial arrangement of these equilibrium positions must consequently be a regular one.

The possible kinds of crystal structure—that is, the kinds of regular arrangement of congruent molecules—were first discussed by Bravais, who described fourteen such kinds of structure, and distinguished them as "space lattices." Bravais's theory, however, only explains seven kinds of symmetry which possess the properties of crystal symmetry, and the incompleteness of his work reposes on the introduction of an unnecessary assumption, namely, that the molecules occupy parallel positions. Sohncke discarded this assumption in attacking the problem, and merely sought for those arrangements of congruent molecules in which the arrangement of parts is the same about every molecule; he thus arrived at sixty-five regular "point systems." By the discovery of these most, though not quite all, of the symmetrical relationships of the properties of crystals became explicable. Sohncke further developed his theory of crystal structure by introducing the assumption that two or more regular point systems, consisting of different kinds of molecules, may be interlaced or supposed to interpenetrate in such a way that equilibrium results. This, however, is only possible when the different point systems possess the same "coincidence movements" (*Deckschiebungen*)—that is to say, when they are built up from space lattices of identical dimensions. This form of the theory is also deducible from the theory of regular point systems if the different individual atoms constituting the molecule are considered in place of the centres of gravity of the molecules; each set of analogous atoms then form a regular point system, and, by the interlacing of the several systems, a compound system is obtained consisting of as many component systems as there are atoms in the chemical molecule. This, the most general theory of crystal structure, may be summarised by the following definition:—

A crystal—considered as indefinitely extended—consists of n interpenetrating regular point systems, each of which is formed from similar atoms; each of these point systems is built up from n interpenetrating space lattices, each of the latter being formed from similar atoms occupying parallel positions. All the space lattices of the combined

* Read before the British Association (Section B), Cambridge Meeting, 1904.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

system are geometrically identical or are characterised by the same elementary parallelepipedon.

In this form the theory is capable of elucidating all the observed regularities of crystal structure, and it is unnecessary to assume the operation of any "molecular forces" in addition to the forces which act upon the atoms themselves. No difficulties now arise in ascribing to the atoms the power of assuming a definite orientation, since, according to J. J. Thomson, the atoms are not mere points, but highly complex structures.

If a crystal is built up from but one kind of atom it consists of a crystalline element, and is produced from but one kind of regular point system the properties of which depend upon the forces exercised upon each other by the similar atoms involved. In the case of a chemical compound, however, there must be just as many regular point systems in the combined system as there are atoms in the chemical molecule, and the arrangement of the combined system must correspond with the equilibrium of the forces with which similar and dissimilar atoms act upon each other.

On solution, melting, or evaporation of the crystal the combined system separates into its component and freely moving molecules, and the relative positions in space of the point systems or space lattices, composed from the several kinds of atoms, must therefore be such as to correspond with the arrangement of the atoms in the chemical molecule. The difference between the crystalline and the amorphous state thus consists in that in the latter the chemical molecules have a mutually independent existence, whilst in the crystal the idea attached to the term molecule is different, the molecule being regarded only as a group or assemblage of atoms belonging to several interpenetrating point systems. Such an assemblage can under certain conditions be quite an arbitrary one; thus, the structure of crystalline sodium chloride—making the simplest conceivable assumption—consists of a cubic space lattice of sodium atoms, and a similar space lattice of chlorine atoms, the latter atoms occupying the mean points in the lattice of sodium atoms. It is obviously a matter of quite arbitrary choice with which of the neighbouring sodium atoms a particular chlorine atom will remain combined as a molecule of sodium chloride when the molecules of the latter separate during the passage into the amorphous state by melting, solution, &c. The same considerations naturally hold when, instead of two simple space lattices, two regular point systems consisting of chlorine and sodium atoms are imagined to coalesce. In this case any multiple of the complex NaCl may be regarded as the "molecule," and thus has arisen the failure of all attempts hitherto made to determine the molecular magnitudes of crystalline bodies.

In order to ascertain the crystal structure of a substance with any degree of probability the most complete possible knowledge is required concerning it, such as of its optical properties, its cohesion relationships, the orientation of its different solubility directions (etch figures), and more especially the knowledge of its crystalline form under the most widely differing conditions of formation. If the product of only one crystallisation is examined, the possibility is incurred that the crystals so produced exhibit casual forms developed under quite special conditions of growth; and only by investigating many different crystallisations separated from different solvents under different conditions of temperature, &c., does it become possible to recognise those faces the development of which is most favoured during growth, or, what is the same thing, to learn what planes are parallel to the greatest density of structure. If these planes are taken as the elementary faces, it is always found, not only that they are identical with the cleavage planes, with the most stable planes of twinning, &c., but also that the other forms present on the crystal assume the simplest indices. The greater the number of forms observed upon the crystals so much the greater is the probability of being able to choose the correct elements for the crystal, because the faces most likely to be favoured during the growth of the crystal are those the indices of which are

composed of the simplest numbers. Having found the correct elements of the crystal, it is a simple matter of calculation to ascertain the ratio of the three parameters and the angles of the elementary parallelepipedon upon which the structure of the crystal is built up, and which is therefore a prime characteristic of the structure.

Since the equilibrium in a crystal structure is dependent on the conditions of movement of the component atoms, the stability of the equilibrium must alter with the temperature; and since each form of structure may possess several stable equilibrium positions of different degrees of stability, it follows that a particular crystal structure will assume the most stable of the possible kinds of equilibrium only within a certain range of temperature, constant pressure being assumed. Outside these limits other kinds of arrangement will be in more stable equilibrium, and on exceeding the limits a discontinuous change of all the physical properties of the body will occur; that is to say, a change into another modification of different crystal structure will ensue. Polymorphism, the property of existing in different crystalline phases, must be distinguished from polysymmetry, or the power possessed by pseudo-symmetrical crystals of forming apparently simple crystals of higher symmetry by repeated twinning. Amongst the latter the change into the form of true higher symmetry can indeed take place at a specific temperature, but the change is not accompanied by a discontinuous change in the density and the specific heat. Amongst the truly polymorphous bodies, however, even when the crystalline forms of the several modifications exhibit a certain similarity, so great a dissimilarity still exists between them in physical and crystallographical respects that the various modifications must be referred to quite different elementary parallelepipedons. A difference in the crystal structure is thus introduced, and this may arise from the regular point systems, which compose the combined system, consisting each of one or of several space lattices.

On comparing the polymorphous relationships of two different but chemically similar substances it is found that the temperature (or pressure) limits of the stability of the several modifications are not the same—thus, considering analogous, chloro-, bromo-, and iodo-compounds, it is often observed that the temperatures of change for the chloro- and bromo-compounds are lower than for the iodo-compound, just as is often the case with the melting-points of such analogous substances. As a result totally different polymorphous modifications of the various members of analogous series exist at one and the same temperature.

The foregoing leads to the definite conclusion that the relationships between the crystal structures of two chemically related substances can only be recognised if their corresponding modifications are available for comparison; every chemico-crystallographical comparison of two or more substances must therefore be based upon a study of the polymorphism relationships. If the existence of corresponding modifications is established by such a study, the further complete investigation of these forms leads to the determination of the most probable values of the dimensions of the elementary parallelepipedon of the crystal structure; by taking the planes of the elementary parallelepipedon as the basis for assigning symbols to the crystal faces, the so-called "elements" of the crystal give immediately the angles, α , β , and γ , and the relative lengths $a:b:c$ of the sides of the elementary parallelepipedon. The elements of the two comparable substances being—

1. $a_1 : b_1 : c_1$ and $\alpha_1, \beta_1, \gamma_1$
2. $a_2 : b_2 : c_2$ and $\alpha_2, \beta_2, \gamma_2$

the comparison of the two sets of elements, if all the other necessary conditions are fulfilled, permits the determination of the alteration which ensues in the structure of the crystal 1, if it be converted by substitution into the substance of crystal form 2. This alteration may be regarded as a "homogeneous deformation," because a homogeneous edifice—the crystal structure of the first substance becomes thereby converted into another homogeneous edifice—the

crystal structure of the second substance. The character of this deformation cannot be recognised through the comparison of the axial ratios of the two substances if these are stated in the ordinary way, but can only be ascertained if the axial ratios are expressed in terms of the same unit. For this purpose an exact determination of the specific gravity of the two substances is made and the "equivalent volume" calculated therefrom; the dimensions (parameters) of the elementary parallelepiped can then be at once referred to the same unit, namely, to the side of a cubic elementary parallelepipedon of a substance of which the molecular weight is equal to the density (equivalent volume = 1). Such comparable parameters are termed the "topical axial ratios," and are described as χ , ψ , and ω . The comparison of the following substances may be quoted as a simple example:—

Ammonium iodide crystallises in hexahedra and exhibits a perfect cleavage parallel to {100}, so that its crystal structure is undoubtedly hexahedral or cubic. Tetramethylammonium iodide crystallises in the tetragonal system, and shows perfect cleavages parallel to {100} and {001}; its most probable crystal structure therefore differs from that of ammonium iodide only in the ratio of the axes a and c . The direction in which the crystal structure has been altered by the substitution of $4H$ by $4CH_3$ is seen by a comparison of the topical axial ratios; as the following table shows, the principal axes c has undergone no noteworthy change, but the parameter of the two axes a and b is much greater in the methylated compound. Tetraethylammonium iodide is similarly tetragonal, and exhibits a regular increase of the parameter of the two equal axes in the same direction; the increase in the equivalent volume is also quite regular during the transition from $4H$ to $4CH_3$ to $4C_2H_5$. On further attempting to lengthen the dimension, a and b , by exchanging $4C_2H_5$ for $4C_3H_7$, a quite different deformation comes into play. As a result of this ψ increases, and χ and ω decrease.

	NH_4I	$N(C_2H_5)_4I$	$N(C_3H_7)_4I$	$N(C_4H_9)_4I$
Equivalent volume	57.51	108.70	162.91	235.95
$\chi =$	3.860	5.319	6.048	6.093
$\psi =$	3.860	5.319	6.048	7.851
$\omega =$	3.860	3.842	3.686	4.933

The so-called morphotropic relationships between numerous organic substances which have been brought to light during many years past consist mainly in the observation that the substitution of H by CH_3 , NO_2 , OH , &c., gives rise in many cases to but partial changes in the crystalline form. In order, however, to determine the direction of deformation, as has been done above for the alkylated ammonium iodides, all the substances must be studied in accordance with the principles laid down above, and their specific gravities determined; further, in cases in which no morphotropic relationships can be traced it must be ascertained whether the substances compared are not different—non-corresponding—modifications. Regularities from which conclusions can be drawn concerning the position of the atoms or atomic groups in the crystal structure can only be traced as a result of this kind of complete investigation of long series of chemically related compounds. That such conclusions can be drawn is evident from the above example.

The only study of related substances which satisfies all the requirements noted above is to be found in the brilliant work of Tutton on the sulphates and selenates; this relates to the comparatively small changes which result from the replacement of K by Cs , Rb , and NH_4 in so-called "isomorphous compounds." In spite of the smallness of the changes produced, Tutton has been able to establish definite relationships between the atomic weight of the metal concerned and the crystal structure, and his work therefore stands as a sample of the way in which chemo-crystallographical investigations must in the future be carried out for the purpose of determining the mutual relationship of the crystal structure and the chemical substance.

As is well known, isomorphous substances possess the power of forming homogeneous mixtures, and, since in these mixtures the properties continuously change with the composition, they have been described as "solid solutions." Such a miscibility often exists, however, within certain limits between substances possessing totally different crystal structures, so that the solidification curves of the molten mixtures of such substances show just the same relationships as if the mixtures had been made from two truly isomorphous materials. It is therefore incorrect to conclude that two substances are isomorphous from an examination of the melting and solidification curves of their mixtures.

Only those substances which exhibit corresponding crystal structures as a result of their chemical analogy can be regarded as isomorphous; mixed solutions of two such substances may be caused to deposit apparently homogeneous crystals in which the atoms of one element are partially replaced by atoms of another without overthrowing the equilibrium of the crystalline structure. The preservation of the equilibrium will clearly be the more easy the less the differences between the forces determining the crystal structure in the two isomorphous substances, and the less therefore also the difference between the two crystal structures. The proportions of the mixture must be immediately deducible additively from those of the components; thus, for instance, each component must preserve its individual specific gravity in the mixture, as has been shown by the careful investigations of Retgers to be the case.

Lastly, the facts which Kipping and Pope have brought to light in connection with optically active and racemic compounds can be brought into unison with the above discussion on crystal structure. Racemic compounds behave towards the optical antipodes like molecular compounds of the same, the crystalline structure being a combined system of the two enantiomorphous systems, whilst the pseudo-racemic substances stand to the active components in the same relation as polysymmetric substances.

The object of the present paper is to state clearly the point of view in accordance with which previous investigations must be developed in order that generally applicable conclusions can be deduced therefrom.

THE CONSTITUTION OF NICKEL CARBONYL.*

By H. O. JONES, M.D., D.Sc.

THE study of the chemical reaction of nickel carbonyl, first undertaken in association with Professor Sir J. Dewar, has been continued and extended.

Nickel carbonyl reacts readily with hydroxylamine in alcohol solution to give a bluish violet-coloured gum which solidifies on standing in a desiccator, is insoluble to all solvents, and is decomposed by water and acids and on heating to $100^\circ C$. The action of water and of heat on the compound gives rise to new compounds similar in appearance to the original substance, and which react with acids, giving nickel and hydroxylamine salts and carbon dioxide.

These compounds have not been obtained pure enough to give analytical results of any value, but the ratio $Ni : NH_2OH$ in the original compound is found to be $1 : 4.5$, and is probably $1 : 4$.

Hydrazine hydrate reacts in a similar way, and gives a blue-violet solid compound.

The formation of these substances shows that nickel carbonyl can react as a ketonic compound.

Nickel carbonyl reacts with the alkyl magnesium iodide compounds of Grignard, in some cases violently, to produce dark coloured oily and solid substances, which contain nickel, magnesium, and iodine, and are decomposed by acids, yielding a mixture of compounds.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

The product obtained from several aliphatic iodides has been examined, but no pure compound has hitherto been isolated and identified. Some of the compounds produced react with sodium bisulphite, hydroxylamine, and substituted hydrazines, and are very probably ketonic.

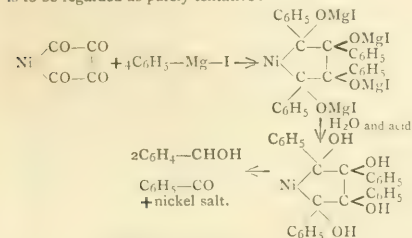
The product of the action of phenyl magnesium iodide on nickel carbonyl when treated with acids gave rise to a mixture which was found to consist chiefly of *diphenyl* and *benzoin*. The former is very readily produced from phenyl magnesium iodide, and is frequently observed among the products of its reactions. The formation of benzoin has an important bearing on the constitution of nickel carbonyl.

All the reactions of nickel carbonyl which have been described previously can be equally well explained by means of either of the two formulæ,—



which have been proposed; but benzoin could be produced in a much simpler way from a compound with the second formula. Its production may therefore be regarded as evidence in favour of this.

The following suggestion as to the course of the reaction is to be regarded as purely tentative:—



The product, $\begin{array}{c} \text{C}_6\text{H}_5 > \text{C}-\text{OH} \\ | \\ \text{C}_6\text{H}_5 > \text{C}-\text{OH} \end{array}$, is supposed to undergo molecular transformation into benzoin.

DUTY-FREE ALCOHOL FOR INDUSTRIAL PURPOSES.

THE Chancellor of the Exchequer has appointed the following gentlemen to serve as members of a Committee to inquire into the use of duty-free alcohol for industrial purposes:—Sir Henry Primrose, K.C.B., C.S.I., chairman; Professor Sir William Crookes, D.Sc., F.R.S.; Sir W. H. Holland, M.P.; the Hon. J. Scott-Montagu, M.P.; Lothian D. Nicholson, Esq.; Dr. W. Somerville; Dr. T. E. Thorpe, C.B., F.R.S.; Thomas Tyrer, Esq.

The terms of reference are:—

“To inquire into the existing facilities for the use, without payment of duty, of spirits in arts and manufactures, and, in particular, into the operation of Section 8 of the Finance Act, 1902; and to report whether the powers conferred upon the Commissioners of Inland Revenue by this section permit of adequate facilities being given for the use of spirits in manufactures and in the production of motive power, or whether further facilities are required; and, if it should appear to the Committee that the present facilities are inadequate, to advise what further measures could be adopted without prejudice to the safety of the revenue derived from spirits, and with due regard to the interests of the producers of spirits in the United Kingdom.”

All communications should be directed to Sir Henry Primrose, K.C.B., at Somerset House, Strand, W.C.

Sir Henry Primrose is Chairman of the Board of Inland Revenue. Sir William Crookes is a Past President of the Chemical Society, and was in 1898 President of the British Association. Sir W. H. Holland is the Liberal member for the Rotherham Division of Yorkshire, and Vice-President of the Associated Chambers of Commerce. The Hon. J. Scott-Montagu is well known for his interest in the use of alcohol for motive purposes. Mr. Nicholson belongs to the Thames Bank Distillery, and is Chairman of the London Distillers' Association. Dr. Thorpe is Director of the Government Laboratories. Dr. Somerville is an Assistant-Secretary at the Board of Agriculture. Mr. Tyrer is Managing Director of the Stirling Chemical Works at Stratford, and is one of the largest manufacturers of alcohol and fine chemicals in the kingdom.—*The Times*.

CONDENSATION OF HELIUM AND HYDROGEN BY CHARCOAL.

By Sir JAMES DEWAR, F.R.S., &c.

In a preceding paper I explained that wood carbon absorbed large quantities of gases at low temperatures, and could be used to produce very high vacua. I have continued my researches on this subject, in order to ascertain the specific behaviour of hydrogen and helium to charcoal when the latter is cooled to the boiling-point of liquid hydrogen.

For this series of experiments I utilised the same apparatus as previously employed for spectroscopic observations, with the addition of a small condenser containing 1 or 2 grms. of wood carbon attached to each of the tubes. Two tubes were filled, one with hydrogen the other with helium, at atmospheric pressure. The little charcoal condensers were now plunged in liquid hydrogen, with the result that the vacuum became so high that no electric discharge would pass in the tube filled with hydrogen.

This experiment is similar to those performed with tubes filled with nitrogen and oxygen, liquid air being used as the cooling agent.

When the tube filled with helium has its charcoal condenser cooled in liquid hydrogen, the vacuum produced is high enough to obtain the phenomenon of phosphorescence under the action of the discharge. After being assured of the absorption of the helium, I put two tubes containing helium from different sources in the liquid hydrogen, and subjected them to the action of liquid hydrogen boiling under exhaustion, and finally attained the temperature of 15° absolute. In each case the vacuum resulting from the occlusion of the helium was so high that a coil giving a spark of 4 c.m. in air had to be used to obtain an intermittent phosphorescent discharge. The tube only gave a continuous spectrum due to the glass.

We may conclude from these experiments that carbon is a good absorbent of helium at 20° absolute, and is a still better one at 15° absolute.

From a number of comparative experiments made with hydrogen it seems that the boiling-point of helium is about 6° absolute.

I intend to continue the experiments, and to find out what the gaseous residue remaining in such tubes can be. The present researches, however, confirm my former conclusions that the boiling-point of helium is not below 5° absolute.

During the course of these experiments, and using the method of condensation by carbon, I have been able to prove the existence of small traces of helium in the gases dissolved in rain-water, sea-water, and even in Thames water.—*Comptes Rendus*, vol. CXXXIX., No. 7, p. 421.

REFRACTIVE INDEX OF CLOVE OIL.

By W. H. SIMMONS.

THE utility of the refractive index in the examination of essential oils has been subject to much criticism, but there can be little doubt that with many oils the figure is a very useful one, and this particularly appears to be the case with clove oil. The principal constituent of this oil is, of course, eugenol, which has a relatively high refractive index, viz., $n_D^{20} = 1.5412$, and I have found, from the examination of several samples of the oil, that with pure oils the refractive index is approximately proportional to the eugenol content, so that—in view of the rapidity with which the determination can be made—it should be of much value to distillers of clove oil, who, I understand, now usually take the specific gravity and phenol content of their finished products. With samples whose genuineness cannot be guaranteed, however, it is not safe to base an opinion on the refractive index only, as is shown by No. 9 in the accompanying table, which is evidently grossly adulterated, judged by the high specific gravity compared with its low proportion of eugenol, though from its refractive index it might be expected to contain about 86 to 88 per cent of phenols.

No.	Specific gravity, $15/15^\circ$.	Rotation, [α] $_D^{20}$.	Refractive index, n_D^{20} .	Phenols, per cent.
1.	1.0606	—	1.5382	93
2.	1.0509	-0° 44'	1.5318	88
3.	1.0506	-0° 53'	1.5304	86
4.	1.0475	-1° 0'	1.5304	86
5.	1.0455	-0° 23'	1.5297	85.5
6.	1.0560	-0° 35'	1.5340	92
7.	1.0549	-0° 40'	1.5340	91.5
8.	1.0507	-0° 54'	1.5336	87
9.	1.0617	-0° 20'	1.5327	82

NOTICES OF BOOKS.

Die Elektrochemische Reduktion der Nitroderivate Organische Verbindungen. ("The Electro-chemical Reduction of the Nitro-derivatives of Organic Compounds"). by JOH. MÖLLER. Halle-a-S.: Wilhelm Knapp. 1904.

THE technical importance of the results obtained on applying the methods of electro-chemistry to organic substances in general is ample justification for the preparation of such a book as this, quite apart from the questions of more purely scientific interest which are discussed in it; and the treatment of nitro bodies may be regarded as a special and important province of organic electro-chemistry, which up to the present has not received sufficient recognition, to judge from the publications exclusively devoted to it which have appeared. This work aims at providing a complete and accurate presentation of the subject both from experimental and theoretical points of view, and it may be said to fulfil its aim admirably. Very numerous results obtained on electrolysis of nitro bodies, both in acid and alkaline solution, are given in it, with all details relating to the performance of the experimental work; also the three theories of Haber, Löb, and Chilesotti, as applied to aromatic substances, are explained and discussed at some length.

Gesammelte Abhandlungen von Robert Bunsen. ("The Collected Works of Robert Bunsen"). Edited by WILHELM OSTWALD and MAX BODENSTEIN. Three Volumes. Leipzig: Wilhelm Engelmann. 1904.

THE German *Gesellschaft für Angewandte Physikalische Chemie* bearing Bunsen's name has commissioned Prof. Ostwald and Dr. Bodenstein to edit this collection of all the great chemist's publications, and in this edition all papers written by Bunsen are arranged in approximately

chronological order. It includes also the whole of the second edition of his "Gasometrische Methoden" which first appeared in 1857. The speech delivered before the London Chemical Society by Sir Henry Roscoe shortly after Bunsen's death contains a specially interesting account of his life, with some correspondence which passed between the two chemists, and it need hardly be said that it gives a very sympathetic view of his life and work. The notices which appeared in the *Zeitschrift für Anorganische Chemie* and in the *Zeitschrift für Elektrochemie* on the occasion of his death are also included. Inasmuch as the value of Bunsen's contributions to our knowledge of physics and chemistry are thoroughly recognised, and his work runs little risk of being under-estimated, such a collection as this calls for no special criticism, for it goes without saying that it will recommend itself to all who are interested in chemistry, and will well repay perusal in the amount of information and instruction which it will be found to contain.

Practical Chemistry. By P. A. ELLIS RICHARDS, F.I.C. London: Baillière, Tindall, and Cox. 1904.

THIS small book has been written specially for the use of students of medicine and dentistry, and contains all that is required by candidates for the Conjoint Board Preliminary Scientific Examination, besides additional matter for the Preliminary Scientific of London University. Thus it includes the qualitative analysis of simple salts and easy mixtures, with a few very useful notes on some salts presenting special difficulties, and also describes the preparations of certain salts as required in the syllabus of the Conjoint Board, besides a few others. The section on volumetric analysis is wonderfully clearly written, and no beginner could fail to understand the explanations in this part, which is on the whole the best in the book. The pages on elementary practical toxicology contain an account of the general reactions of the more common poisons, with a description of the methods used for the detection of a poison, both in a simple solution and also an organic mixture.

Die Neuren Strahlungen. ("The Newer Rays"). By HANS MAYER. Second Edition. Mähr-Ostrau: R. Papauschek. 1904.

THIS short account of the theoretical and experimental results obtained during the investigation of the cathode, canal, and Röntgen rays, and the phenomena of radio-activity generally, is clearly written and eminently readable; the facts and theories stated in it are judiciously chosen and well balanced, and the work of various investigators is very fairly described, so that the reader ought to get a good idea of the real part played by the several workers in the development of the most modern theories. The book is more scientific than the usual run of popular expositions of this kind, and even the uninitiated reader will gather from it some clear ideas of the new theories regarding the constitution of matter and of the theory of electrons. The chief fault to be found with it is the author's disregard for the need of constantly emphasising the very important difference between results which may be safely regarded as thoroughly well established and others which are still in dispute; as, for example, in the case of the wave-length measurements of X-rays and the atomic weight of radium. However, the book has evidently met with some success, for the first edition was exhausted within a month from its appearance.

Das Königliche Materialprüfungsamt der Technischen Hochschule, Berlin. ("The Royal Testing Office of the Technical High School at Berlin"). By A. MARTENS and M. GUTH. Berlin: Julius Springer. 1904.

THIS volume, prepared in commemoration of the opening of the new buildings at Gross-Lichterfelde West, gives an elaborate description of the working of this department of the Technical High School at Berlin. The arrangements

of the buildings are fully explained, and an account of the history of the department given at great length. The communications which have issued from the institution during the years 1883 to 1903, which give a good idea of its great activity, are enumerated and indexed, and numerous tables and statistics are contained in the text. The descriptions of the laboratories and their appliances, which are copiously illustrated by photographs and plans, will be found to contain many useful hints for those who are interested in the fitting-up of similar institutions, the very latest improvements in structure and arrangement having evidently been adopted in this most palatial building. The enlarged space now at the disposal of the institution will give its workers increased opportunities of energetically extending the valuable work which is being done in it, especially on the purely scientific side, the importance of which is duly recognised; and the chapter at the end of the book on the aims of the institution for the future shows the standard of usefulness which the Director has put before him, and the special means which are to be taken to come up to this high standard. It is evident from the whole book that nothing could be done to add to the convenience of those who are engaged in this department of the Technical Hochschule, for they are surrounded by the most favourable circumstances for doing work of permanent and high scientific value.

Fortieth Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. London: Printed for His Majesty's Stationery Office by Messrs. Eyre and Spottiswoode. 1904. Pp. 183.

THIS report, under the Alkali, &c., Works Regulation Acts of 1881 and 1892, comprises the proceedings during the year 1903, presented to the Local Government Board and to the Secretary for Scotland.

The number of works now registered under the Acts in England, Ireland, and Wales is 1034. Of these 75 only are works decomposing salt, and so scheduled as alkali works, while the remaining 959 carry on processes which are scheduled or subject to registration. There are also 127 works registered in Scotland, bringing the total number of works registered in the United Kingdom to 1161.

During the year 1903, the total number of visits made by the Inspectors was 4838, while 5211 tests were made, and in only one case was it necessary to take proceedings for recovery of penalty for infraction of the provisions of the Act. A severe escape of noxious and offensive gases of very acid and irritating character was found at a chemical manure works; the plant was in a totally unfit condition for work, being much out of repair.

A Bill to amend and consolidate the Alkali Acts was read a first time in the Session of 1903; various conferences were held during the recess, as the result of which a new Bill was presented in 1904.

Viewed as a whole it may be said that the conduct of the Alkali and Wet Copper Works, the longest under inspection under the Alkali Acts, has given little ground for complaint. For individual cases, however, there has been much ground for anxiety, and serious representations had to be made in three cases, that if the escape of muriatic acid was continued penalties would be pressed for.

There has been almost complete absence of complaint during the year of escape of chlorine gas from the large manufacturing operations in which it is evolved and subsequently absorbed.

An interesting and valuable investigation has been conducted by Mr. Linder, to determine the conditions most favourable for the complete absorption of H_2S and SO_2 by "waste" slurry, either alone or in conjunction with added lime; this is given in detail on pp. 13-18.

The average escape of acid gases of sulphur and nitrogen from exits of sulphuric acid works, in which this manufacture is carried on by the lead chamber process, is still maintained at a figure that must be regarded with satisfaction, as indicating the continued care and attention that, in a large number of works, are devoted to the conduct of

this manufacture on the best and most economic lines. The average escape of the 211 exits tested varies but slightly from the figures already given for the years 1901 and 1902, viz., 1.248 grains of SO_2 per cubic foot.

The results of the investigation presented in last year's report on the testing of acid gases escaping from the chamber process of sulphuric acid manufacture have received some attention at the hands of manufacturers, and through the courtesy of Messrs. Chapman, Messel, and Co., of Silvertown, Mr. Linder has been enabled to prosecute some further investigations on the reactions in the sulphuric acid chambers and connections at various points, with the view of ascertaining if any evidence could be obtained of the existence at any point in the chamber system of the sulphazotised bodies, hydroximidol-sulphuric or hydroxyamido-sulphuric acids, the latter being one of the products of the hydrolysis of the former.

The important class of work comprising sulphate and muriate of ammonia and gas-liquor works continues to increase in number; the tendency for gas works to manufacture their own residual products in place of disposing of the crude materials is certainly on the increase, and it is pointed out that the number of such processes forms the largest contribution by far to the total of 1456.

Through the courtesy of managers, the Chief Inspector is again able to give the figures for the amount of sulphate of ammonia produced in the United Kingdom; these are given on p. 30.

With regard to salt works it is pointed out that the muriatic acid escaping into the atmosphere from this class of works is maintained well within the maximum permitted, viz., one-fifth of a grain per cubic foot of chimney gases. The expectation that during 1903 some opportunity of observing the results of applying gaseous firing to salt pans has not been fulfilled; the plant, however, is in a forward state of preparation.

CORRESPONDENCE.

PATENT LAW, 1902.

To the Editor of the Chemical News.

SIR,—The Board of Trade has just issued an order bringing into force on January 1st next the Government examination system for patents set forth in the Patent Law of 1902, and from January 1st, 1905, reducing the period of provisional protection from nine months to six. The system of examination thus instituted is much less perfect than those of other countries, as the Examiner has merely to search through the British patents of the immediately preceding fifty years to see if in these there be, in his opinion, any anticipation of the invention set forth in the complete specification. This report is forwarded to the Comptroller, and if the Comptroller be of the opinion (from this report) that the invention is partly or wholly anticipated, the applicant is informed of the anticipation, and has the option of a personal hearing, or of amending the specification to the satisfaction of the Comptroller, or in default of either, the Comptroller determines whether a reference to any and if so what prior specifications must be made in the specification by way of notice to the public. Against his decision there will be an appeal to the Law Officer. The Examiners' reports will be kept strictly secret from all but the applicant and his agent, but this examination must not be held in the slightest to guarantee in any way the novelty of the invention or the validity of the patent, as of course the prior publication of the invention in other documents open to the public in England prior to the date of the application, or the prior public use of the invention, would be equally as fatal to the validity of the patent as the publication of the invention in a prior British specification.—We are, &c.,

W. P. THOMPSON and Co.,
Chartered Patent Agents.

6, Lord Street, Liverpool,
Sept. 1st, 1904.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

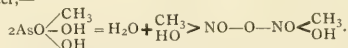
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 6, August 8, 1904.

Theory of Dilute Solutions Based on van't Hoff's Law.—E. Ariès.—By applying the phenomena of osmosis to dilute solutions M. van't Hoff deduced a law from which a complete theory of such solutions can be evolved.

Vanadium Steels.—Léon Guillet.—The author's researches on the subject of vanadium steels show:—1. That such steels produced at 900° and slowly cooled are not so fragile as ordinary steels containing the same amount of carbon, and that to the same resistance they are decidedly less fragile; (2) the steels containing a large percentage of vanadium, and in which all the carbon is in the state of carbide, are absolutely heterogeneous. This is most probably due to the vanadium carbide which, pre-existing in the bath and having a very small density, tends to reappear on the surface. In all cases it can be affirmed that the only interesting vanadium steels are those which contain less than 0.7 per cent of vanadium.

Certain Derivatives of Pentabasic Phosphoric Acid.—P. Lemoult.—When PCl_5 is totally anilinated the only tetranilide product obtained is of the type $\text{Cl}-\text{P}(\text{NHR})_4$. The reactions of such compounds with regard to sodium alcohols vary with the nature of R. If R is a phenyl the phosphonitrated base $\text{C}_6\text{H}_5-\text{N}=\text{P}(\text{NHC}_6\text{H}_5)_3$ is obtained. If, on the contrary, R is a homologue of phenyl (e.g., *o*-tolyl or *m*-xylyl) the products obtained vary with the alcoholate used whilst keeping the same general properties. These are the arylamide-phospho ethers of formula $\text{R}'-\text{O}-\text{P}(\text{NHR})_4$, where R' is an alcoholic radical.

Dimethylpyroarsenic Acid.—E. Baud.—The author proves the existence of a pyroarsenic acid corresponding to pyroarsenic acid, which is prepared by heating anhydrous monomethylarsenic acid on an oil-bath at 130°–140° in a current of dry hydrogen, when it loses half a molecule of water,—



The compound obtained is dimethylpyroarsenic acid. This acid decomposes on a rise of temperature into methylic alcohol and arsenious anhydride.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxxi., No. 3.

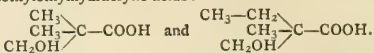
Influence of Gases on the Separation of Metals by Electrolysis. Separation of Nickel and Zinc.—MM. HOLLARD and BERTIAUX.—Already noticed.

The Optical Activity of Cellulose and its Nitrated Derivatives.—Leo Vignon.—The optical activity of cellulose has been examined by Bechamp and Levallois who found contradictory results; the latter chemist found that it was levogyre, while the former declared it to be inactive. The author concludes from his experiments that the question of deciding the optical activity of cellulose in its original state is not yet solved. He shows that, on the other hand, dinitro-oxycellulose (with C_6) is a dextrogyre substance, and he has measured its rotatory power in an ether-alcoholic mixture and in acetone.

Determination of the Carbonate of Sodium necessary for the Precipitation of the Lime and Magnesia in the Chemical Purification of Water.—Leo Vignon.—Already noticed.

The α -Dialcylhydropyridic Acids.—E. E. Blaise and L. Marcilly.—This paper deals chiefly with the α -dialcyl-

hydropyridic acids, and among them oxypivalic and α -methylcylhydropyridic acids:—



The author commences with the condensation of bromoisobutyrate of ethyl with trioxymethylene in the presence of zinc. The condensation takes place very easily when the conditions are favourable. It is even necessary to check the reaction by cooling the flask, otherwise the condenser would not be able to condense the whole of the benzene. A series of operations was made with 1000 grms. of bromoisobutyrate of ethyl, and the author obtained 391 grms. of an ether passing over at 84°–86° under 16 m.m., 19.5 grms. passing over at 110°–116° under 12 m.m., 50 grms. passing over at 150°–166° under 15 m.m., and 40 grms. of undistillable residue from which he has not been able to isolate any body. He has examined the above fractions, and describes them in full.

Oxypivalic Acid.—L. Marcilly.—The author has already described the preparation and purification of pure oxypivalic acid. Its constitution has been determined by oxidation, and the complete oxidation furnishes dimethylmalonic acid. The author has examined a large number of derivatives and compounds of oxypivalic acid, and describes them all in a very long paper.

A New Triiodised Phenol.—P. Brenans.—Already noticed.

The Oxidation of Orthonitrotoluene.—C. Lauth.—The author has conducted a series of experiments with the object of preparing ortho-nitro aldehyde from ortho-nitro toluene, and though he did not succeed in his attempt he observed several facts which are of interest. Among the numerous transforming reagents tried, only the acid oxidisers gave the aldehyde; this substance was not obtained either with the alkaline or neutral oxidising agents, with the exception of ozone.

The Phthalate and Mellate of Bismuth and Pyrophosphoric Bismuth.—Paul Thibault.—The three phthalic acids do not all react in the same manner on oxide of bismuth, still they have a common property; they do not act on the hydrated oxide of bismuth, and the orthophthalic acid only acts on the anhydrous oxide, while the isophthalic and terephthalic (meta and para) acids leave this oxide unattacked. To obtain phthalate of bismuth, the anhydrous oxide is treated with an excess of orthophthalic acid in the presence of boiling water for ten or twelve hours; at the end of this time a microscopic examination no longer reveals the presence of opaque yellow needles of the anhydrous oxide; filter hot, and wash with strong alcohol, or better with a mixture of alcohol and ether. A white crystalline body is left, decomposed by water, insoluble in the ordinary solvents, soluble in the mineral acids with the liberation of phthalic acid, and the formation of a corresponding salt of bismuth. Mellic acid in aqueous solution of moderate strength acts very rapidly when heated on both the anhydrous and the hydrated oxides of bismuth. The product is a white crystalline body not decomposed even by boiling water or alcohol, &c. By decomposing crystallised mellate of bismuth by heat *in vacuo* a pyrophosphoric bismuth was obtained.

Detection of Acetone in Urine.—M. Vournasos.—Minimal quantities of acetone can be detected in urine by means of the same reagent already described for the detection of lactic acid in gastric juice. This reagent is a solution of iodine in methylamine or aniline. It acts on acetone in the same manner as on lactic acid; that is to say, in alkaline solution it causes the formation of iodoform, which simultaneously enters into combination with the nitrogen of the amine, giving rise to an isonitrite; in this case the isocyanide of methyl (methylcarbonylamine).

Estimation of Organic Matters in Water. Drawbacks to the Use of Filter-papers before Analysis.—C. Lenormand.—Already inserted in full.

MISCELLANEOUS.

Important Experiments in Radio-activity.—We are indebted to the *Chemist and Druggist* for the following important cablegram from their Representative in New York:—

"New York, September 12.

"Since the Banquet at the Waldorf-Astoria, Sir William Ramsay has courteously revised for me my version of the important statement which he then made. I therefore add this to my previous messages:—

"Sir William Ramsay says experiments are in progress [in the University College Laboratories—Ed. C. & D.] with radio-active substances, the results of which seem to show that we are on the brink of discovering the synthesis of atoms. This may lead us to the discovery of the ordinary elements. These may be the products of the breaking-down of radio-active elements of high atomic weight, as when radium changes into helium."

Estimation of Tannin with Ferric Salts.—M. RUOSS. —The German Commission for the Unification of the Methods for the Estimation of Tannin in 1883 adopted officially the Loewenthal-von Schroeder process. This process consists of determining the difference of the oxidising power between the raw solution and the solution filtered through powdered skin. Now, powdered skin absorbs a considerable amount of colouring matter which acts on permanganate. The amount of cameleon used is not, therefore, in proportion to the real amount of fixed tannin. The author proposes to precipitate the tannin by means of a ferric salt under definite conditions. A tannate of iron is formed of constant composition; the amount of tannin it contains is deduced from the weight of oxide of iron obtained on calcination. *Reagents.*—(1) Solution of crystallised carbonate of soda (71·36 per thousand); (2) solution of ferric sulphate at 50 grms. per litre; (3) solution of 5 grms. of tartrate of soda in 1 litre of acetic acid at 30 per cent. The method of working is as follows:—Fifty c.c. of a solution of tannin (about 4 grms. per litre) are treated with 10 c.c. of carbonate of soda and 10 c.c. of ferric solution, then with 25 c.c. of acetic tartrate of soda. Boil, filter, and wash with warm water. The precipitate is dried and calcined; the sesquioxide of iron is weighed. The weight found, multiplied by 4·024, gives the proportion of tannin in the 50 c.c. taken.—*Zeit. Anal. Chem.*, vol. xli., p. 717.

PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Post of STEWARD in the Chemical

Laboratories of the School of Pharmacy is now vacant.—Applications, stating age and experience, and accompanied by one or more testimonials, should be sent at once to Professor CROSSLEY, 17, Bloomsbury Square, London, W.C.

UNIVERSITY OF GLASGOW.

ADDITIONAL EXAMINERSHIPS.

The University Court of the University of Glasgow will shortly proceed to appoint the following additional Examiners:—

- (a) For Degrees in Arts and Science.—One Examiner in MATHEMATICS and NATURAL PHILOSOPHY. Annual salary, £60.
- (b) For Degrees in Arts, Science, and Medicine.—One Examiner in CHEMISTRY. Annual salary, £50.
- (c) For Degrees in Medicine and Science.—One Examiner in PHYSICS. Annual salary, £50.

The appointments will be for three or four years from January 1st, 1905, and, in addition to the above-mentioned salaries, hotel and travelling expenses will be paid.

Candidates should lodge twenty copies of their application and testimonials with the undersigned on or before NOVEMBER 12th, 1904.

ALAN E. CLAPPERTON,

91, West Regent Street, Secretary, Glasgow University Court, Glasgow.

SOUTH-WESTERN POLYTECHNIC,

MANRESA ROAD, CHELSEA, S.W.

Principal—S. SKINNER, M.A.

THE TECHNICAL COLLEGE re-opens

OCTOBER 3rd, 1904.

THE ENTRANCE EXAMINATION will be held on SEPTEMBER 19-20, 1904.

Three Free Studentships of the value of £45 are awarded on the results of this Examination.

The Courses are divided into two Sections:—

- (1) LONDON UNIVERSITY COURSES; and
- (2) TECHNICAL COURSES.

LONDON UNIVERSITY COURSES.

These Courses are designed to prepare Students for the London B.Sc. Degree in the subjects mentioned below:—

Matriculation Course (one year) . Fee, £12 10s. per Session.

Intermediate Science Course (one year) £15 ..

B.Sc. Courses by recognised Teachers for Internal Students of two years' duration in the following subjects:—Mechanical and Electrical Engineering, Mathematics, Physics, Chemistry, Botany, and Geology.

Fee for the Engineering or Science Degree Course, £15 per Session.

TECHNICAL COURSES.

These Courses are of three years' duration, and give a thorough training to those who wish to become Electrical or Mechanical Engineers, or Consulting or Industrial Chemists.

Electrical Engineering . . . Fee, £15 per Session.
Mechanical Engineering . . .
Applied Chemistry . . .

Further information may be obtained from the Day Prospectus, price 1d., by post 3d.

Complete EVENING COURSES are also provided, of which full particulars may be obtained from the Evening Prospectus, price 1d., by post 3d.

BOROUGH POLYTECHNIC INSTITUTE,

103, BOROUGH ROAD

(Close to the Obelisk, Blackfriars Road, S.E.).

EVENING CLASSES (LECTURES AND PRACTICAL LABORATORY WORK), commencing MONDAY, OCTOBER 3rd, 1904.

CHEMISTRY.—F. MOLLWO PERKIN, Ph.D.,

Assisted by H. B. LAW, B.Sc., and A. J. HALE.

INORGANIC.—Elementary: Tuesdays and Thursdays, 7.30—10. Advanced: Mondays and Wednesdays, 7.30—8.30. Special and Honours: Lectures—Mondays, 7.30—8.30; Laboratory—Mondays, Tuesdays, Wednesdays, and Fridays. Fees, 10s. to 15s.

ORGANIC.—Elementary: Tuesdays and Thursdays, 7.30—10. Advanced: Mondays and Wednesdays, 7.30 to 10. Honours: Lectures—Tuesdays, 8.30—9.30; Laboratory—Monday, Tuesday, Wednesday, and Friday. Fees, 10s. to 20s.

ELECTRO-CHEMISTRY.—Lectures—Fridays, 7.30—8.30; Laboratory Work—During the day, at times to be arranged. Fee, 70s.

SATURDAY MORNING CLASS FOR PRACTICAL CHEMISTRY, 9.30—1. Fee, 10s.

ELECTRICITY & MAGNETISM.—JOHN

HENDERSON, D.Sc., A.I.E.E., assisted by H. S. SAUNDERS.

ELEMENTARY (Lectures and Laboratory)—Mondays, 7.30—10. **ADVANCED COURSE.**—Tuesdays, 7.30—10.

HONOURS COURSE.—Mondays, 9.10—Wednesdays, 7.30.

ELECTRICAL AND MAGNETIC MEASUREMENTS.—Fridays, 7.30—10.—This Course is intended for Electrical Engineers, Instrument Makers, and others engaged in Electrical Work. Fee for the Session, 10s. and 12s.

Full particulars may be obtained on application.

C. T. MILLIS, Principal, Education Department.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Prices 1/6 each (post free 1/8). Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume
16, NEWCASTLE ST., FARRINGTON ST., E.C.

THE SIR JOHN CASS TECHNICAL INSTITUTE.
JEWRY STREET, ALDGATE, E.C.

Principal—CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.

EVENING CLASSES IN CHEMISTRY, METALLURGY, PHYSICS, and MATHEMATICS.Designed to meet the requirements of those engaged in
CHEMICAL, METALLURGICAL, and ELECTRICAL
INDUSTRIES,
and in trades associated therewith.Also preparation for the B.Sc. Examination of London University.
Every facility for Special and Advanced Practical Work in well-
equipped Laboratories, both in the Afternoon and Evening

CHEMISTRY	CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.
PHYSICS.	R. S. WILLOWS, D.Sc., M.A.
METALLURGY.	C. O. BANNISTER, Assoc.R.S.M.
MATHEMATICS.	G. M. K. LEGGETT, B.A.

CLASSES IN METALLURGY.

GENERAL METALLURGY.

THE METALLURGY OF GOLD, SILVER, and LEAD.

FUEL and REFRACTORIAL MATERIALS.

METALLOGRAPHY, including PYROMETRIC WORK.

ASSAYING.

ANALYTICAL CHEMISTRY.

Including ELECTROLYTIC and GAS ANALYSIS.

Each Course of Lectures will be accompanied by suitable Laboratory Work.

GLASS BLOWING.

A series of Courses of Instruction will be given during the Session by Mr. A. C. COSSOR.

NEW SESSION begins MONDAY, SEPT. 26th.The Institute is readily accessible, and near to Fenchurch Street, Liverpool Street, Broad Street, and Metropolitan Railway Stations.
For details of the Classes apply at the Office of the Institute, or by letter to the PRINCIPAL.W. H. DAVISON, M.A.,
Clerk to the Governing Body.**THE POLYTECHNIC,**

309, REGENT STREET, W.

UNIVERSITY OF LONDON PREPARATION CLASSES.

Full Courses of Instruction for Matriculation,Inter. Arts, Science, and Engineering, and Final Arts.
Special Courses for Final B.Sc. in Mathematics, Physics, and Chemistry.

Examinations are held at the above Institute.

NEXT TERM commences SEPTEMBER 16th, 1904.

Courses are so arranged that Students can do the work on Saturday and one evening per week.

Full particulars can be obtained on application to the DIRECTOR OF EDUCATION.

CITY OF LONDON COLLEGE,WHITE STREET and ROPEMAKER STREET,
MOORFIELDS, E.C.**MICHAELMAS TERM commences OCTOBER 3rd.****CLASSES and LABORATORY WORK in**
CHEMISTRY, PHYSICS, BIOLOGY, BOTANY,
GEOLOGY, and PHYSIOLOGY. Special preparation for the
Examinations of the Pharmaceutical Society, The Conjoint Board.
Complete Courses for University Matriculation and Inter. and Final
B.Sc., meeting during the Evening and on Saturday.

Full particulars gratis on application to—

DAVID SAVAGE, Secretary.

REDRUTH SCHOOL OF MINES, CORNWALL.**Session 1904-1905 begins September 7th.****A "Mining Certificate" is awarded to Students**
passing successfully through the School Course.**PRACTICAL MINING CLASSES**, under the instruction of
Capt. WILLIAM HAMBLEY (late Government Inspector, South Africa)
Distinctions in Mine Surveying in Open Examination five years in
succession, including five Medals and Prizes, being all the awards of
the City and Guilds of London Institute in 1904 in this subject.SYLLABUS and every information on application to—
THE REGISTRAR.**RADIUM BROM.****POLONIUM.****RADIO-ACTIVE ORES.****BAR.-PLAT.** CYAN.
SCREENS." LARGE CRYSTALS.
ETC., ETC.,**ALL AT REASONABLE PRICES.****Armbrrecht, Nelson & Co.,**

71-73, Duke-st., Grosvenor-sq., W.

'Phone—1942 Gerard.

CARPENTERS' COMPANY'S**TECHNICAL INSTITUTE,**

JUPP ROAD, STRATFORD, E.

CLASSES

IN

SCIENCE, ART, TECHNOLOGY, and
LANGUAGES.

Chemical and Physical Laboratories.

Manual Training.

Workshops for PLUMBING, ENGINEERING, CARPENTRY
and JOINERY, &c., WOOD-CARVING.**OPENS on MONDAY, SEPTEMBER 19th.**

Prospectus on application.

EAST LONDON TECHNICAL COLLEGE,

MILE END ROAD, E.

Session 1904-1905, commencing September 19, 1904.**DAY and EVENING COURSES for the**
B.Sc. (Honours and Pass) Degree of the University of London
are conducted by the following Lecturers, who are recognised teachers
of the University of London:—

Mathematics	J. L. S. HATTON, M.A., and
Physics	W. F. S. CHURCHILL, M.A.
Chemistry	R. A. LEHFELDT, D.Sc., &c.
Botany	J. T. HEWITT, D.Sc., Ph.D., and
Engineering	C. SMITH, D.Sc.
Electrical Engineering	V. H. BLACKMAN, M.A.
	D. A. LOW, M.I.E.E.
	J. T. MORRIS.

The Day Courses in ENGINEERING and CHEMISTRY are
also suitable for those entering manufacturing firms.

Calendar 25d. post free on application.

J. L. S. HATTON, Director of Studies.

THE CHEMICAL NEWS.

VOL. XC., No. 2339.

THORIUM; CAROLINUM, BERZELIUM.*

By CHARLES BASKERVILLE, Ph.D., F.C.S.

Synopsis.

THIS paper presents a brief historical account of the discovery of thorium and the questions raised as to its elementary character.

The published evidence is considered in conjunction with experimental data obtained, and the conclusions arrived at that thorium is not a primary radio-active body.

The complex nature of thorium is proved by the conduct of salts with certain organic bases, as phenylhydrazine, for example. Fractions were added giving atomic weights from 212 to 252, the original being 232.5.

Pure thorium oxide from several sources was converted into the chloride by heating it, mixed with pure sugar carbon within quartz tubes, during the passage of dry chlorine. A volatile chloride, "weisser dampf" of Berzelius was obtained, decreasing in amount according to the duration and temperature of the reaction. The purified, delicately green oxide obtained from this gave a specific gravity of 8.47, and the element berzelium an atomic weight of 212 (tetrad).

The temperature of the porcelain tube was raised and thorium tetrachloride distilled away. The residue in the carbon boat on purification gave a greyish pink oxide with a specific gravity of 11.26 and an atomic weight of (tetrad) 255.6 (carolinum). The new thorium, or that in a large measure freed from the berzelium and carolinum, gave an atomic weight of 220.6, and a white oxide with a specific gravity of 9.2. The original thorium gave atomic weights 232.5 to 232.6, and its oxide had a specific gravity of 10.5.

The original thorium dioxide phosphoresces under the influence of ultra violet light, as does zirconium dioxide. Berzelium and carolinum oxides do not respond to this stimulus, while the new thorium glows with increasing luminosity according to the decrease of the novel substances. All these bodies are radio-active.

Certain chemical differences are noted, as, for example, the conduct of their salts with organic bases, fumaric acid, &c. Carolinum oxide is soluble in concentrated hydrochloric acid, while berzelium and thorium oxides are not.

Spectral data are wanting; in fact, the limited portions of the spectra (arc and spark) mapped show the bodies identical. The materials are not yet sufficiently pure, nor the spectral data sufficiently complete, to warrant final acceptance, although the preponderance of evidence is favourable to the assumption of the existence of two new members of the family of chemical elements.

The marvellous phenomena of radioactivity, accounts of which have filled our chemical and physical literature for the past six years, have stimulated numerous investigators to take part in asking a solution which would be satisfactory, and not wholly drive us from our former conceptions of the fundamental laws of the conservation of matter (whatever it may be) and energy (however we may measure it). Naturally such have had to do with thorium, the radio-activity of which was independently noted by G. C. Schmidt (*Wied. Ann.*, 1898, lxx., 141) and Curie (*Comptes Rendus*, cxxvi., 15; see also Mme. Curie's Thesis presented to the Faculté des Sciences de Paris, 1903), and studied extensively from both points of view by Rutherford, Soddy,

and their co-workers (many papers in *Philosophical Magazine*; *Proc. Chem. Soc.*, 1902, xviii., 2, and *Transactions*, 1902, lxxxi.-lxxxii., 476, &c.), Giesel (*Ber.*, 1901, xxxiv., 3776), Hofmann and Zerban (*Ber.*, 1902, xxxv., 533 and 1457, and xxxvi., 3093), Owens (*Phil. Mag.*, October, 1899), Pegram (*Physical Review*, 1903, xvii., 424), and others, as well as myself (*Journ. Am. Chem. Soc.*, 1901, xxiii., 761).

Other communications upon our researches on thorium have been withheld in the hope of early reaching a solution of the difficult problems involved in an investigation of that element. While the work is far from complete—is any scientific work complete?—we think sufficient evidence of the complexity of the element has been accumulated to warrant definite statements, and excuse us from having had recourse to that "bastard *a priori* method," according to Herbert Spencer, namely, drawing conclusions from insufficient data. Further, on account of the numerous investigations that are coming out upon the elements of high atomic weights, it is well to offer our observations that they may be of service to others.

(NOTE.—When my first preliminary paper on the complexity of thorium was made known publicly, in a note I gave as an excuse for publishing the work, a statement of the fact that I had written Professor Bohuslav Brauner that I thought I had brought about a breaking down of the element. I requested a sample of the very pure body he had prepared and used in his excellent atomic weight determinations that I might check my work. I received no acknowledgment of the letter, and would not know to this day that it had been received but for what followed. Dr. Brauner shortly published some work which clearly pointed to thorium being composite. Having devoted some years of study to the work myself, and following entirely different lines, I immediately, within eight days, at the first public opportunity, presented my paper. For fear I might be misunderstood, the facts outlined above were made known. In a letter to the Editor of the CHEMICAL NEWS Dr. Brauner took exception to my statement, assuming an intimation on my part that he had taken advantage of information contained in a private letter. The letter, in which I gave no details of the method of procedure, was quoted from (so it was received); furthermore, an excuse was given for not having replied to the letter that I was interfering with his field. Apparently a large number have interfered with that field since my publication. I purposed saying nothing regarding Professor Brauner's letter, but on account of the earnest solicitation of many friends the above statements are made known. It was utterly foreign to my mind to cast any reflections upon Professor Brauner. I appreciate most keenly his beautiful researches carried out in the rare earths, in which field that savant ranks as a master. I must object, however, to his having the field reserved. In fact, our work was carried out upon entirely different lines and similar conclusions reached. While it is only human that one should care to have his work appreciated, yet I am not engaged in scientific work for the credit alone).

In 1817 Berzelius ("Afhandl. i. Physik. Kemi. och Mineralogie," vol. v., p. 76; *Ann. Chim. Phys.*, v., 8; *Schweigger's Journ.*, xxi., 25), while investigating gadolinite from Korarvet and another mineral from Finbo, believed he found an unknown oxide similar to zirconia, and called it "thorine," after the mythological Scandinavian god of thunder, Thor. This master chemist, marvellously accurate, especially for the time, soon learned ("K. Vet. Acad. Handl.," vol. ii., pp. 4, 315; J. B. Berzelius, 1824, v., 112) that "thorine" was, in fact, a phosphate of the yttrium earths, and the name properly remained but a short time in chemical literature. In 1828 this same chemist ("K. Sv. Ver. Akad. Handl.," 1829, 11; *Ann. Phys.*, xvi., 388) found a new mineral, thorite, on the Island Lövö, near Brevig, Norway. In it he discovered a new element with which he revived the name thorium. Chydenius ("Kemisk undersökning af Thorjord och Thorsalter," Helsingfors, 1861; *Ann. Phys.*, cxix., 43) com-

* Presented before the New York Section of the American Chemical Society, April 8, 1904.

pleted the investigation, and Cleve (*Bull. Soc. Chim.*, 1874, [2], xxi., 116) revised the older data in 1874. Nilsson, with Krüss and Hillebrand, in many researches determined its atomic weight and secured unquestionable evidence as to its quadrivalence (*Ber.*, 1876, ix., 1056; 1882, xv., 2519, 2521, and 2537; 1883, xvi., 153; 1887, xx., 1665; *Ztschr. Phys. Chem.*, 1887, i., 301, &c.). Quite recently Wyruboff and Verneuil (*Bull. Soc. Chim.*, 1899, [3], xxi., 118), for reasons we need not enter into here, brought up the question of the quadrivalence of thorium which really depended largely upon the specific heat values obtained by Nilson (*Ber.*, 1883, xvi., 153). Biltz (*Liebig's Ann. Chem.*, 1904, cccxxi., 334) appears to have settled the matter by a rigid examination of the thorium acetylacetonate of Urbain (*Bull. Soc. Chim.*, 1896, [3], xv., 347).

In 1851 Bergemann (*Ann. Phys.*, 1851, lxxxii., 561) claimed to have found the oxide of a new element, "donarium," in the yellow variety of thorite, orangite, studied independently by himself and Kraut (*Ann. Phys.*, lxxxii., 568; *Liebig's Ann. Chem.*, 1851, lxxx., 267). Damour, the year following (1852), showed that donarium oxide was impure thorium oxide containing lead and uranium (*Ann. Phys.*, lxxxv., 555; *Liebig's Ann. Chem.*, 1852, lxxxv., 237). Bergemann shortly after observed that donarium and thorium were the same (*Ann. Phys.*, lxxxv., 556; *Liebig's Ann. Chem.*, lxxxv., 239). Berlin (*Ann. Phys.*, lxxxv., 556; lxxxvii., 608; *Liebig's Ann. Chem.*, 1852, lxxxiv., 238) arrived at the same conclusion, as did Delafontaine in 1863 (*N. Arch. Phys. Nat.*, xviii., 343; *Fahresher.*, 1863, p. 197).

Again in 1862 was thorium mistaken for a new element, namely, wasium, reported by Bahr in waste from Rönsholm ("Oefvers of K. Vet. Akad. Förhandl.," 1862, p. 415; *Ann. Phys.*, cxix., 572). The properties were very similar to those of thorium. Its existence not being clearly defined Nickles investigated it, maintaining it was a mixture of yttrium earths containing didymium and terbium (*Comptes Rendus*, lvii., 740). Delafontaine (*N. Arch. Phys. Nat.*, xviii., 369; *Fahresher.*, 1863, p. 201) insisted that it was a mixture of cerite earths, and Popp (*Liebig's Ann. Chem.*, cxxii., 364) asserted that it was nothing else than yttrium containing cerium. The discoverer shortly announced its identity with thorium, and proved its hypothetical existence (*Liebig's Ann. Chem.*, 1864, cxxii., 227).

There are not a few instances in the history of chemistry where scientific interest in some particular element or compound has been stimulated directly or indirectly through its commercial application and the demand thereby created. This is particularly true of thorium. The first German patent issued, Auer von Welsbach, marks the creation of unusual interest in the main constituent of his mantle (*Moniteur Scientifique*, 1894, [4], viii., 2, Patent List, p. 136, &c.). The improvement in the methods for its extraction on a large scale soon opened the gates wide for numerous researches. Although defined with precision through the work of those mentioned, Nordenskiöld (*Fahresher.*, xiii., 134), Petterson (*Comptes Rendus*, xci., 232), Troost and Ouyard (*Comptes Rendus*, cii., 1422), Berlin (*Pogg. Ann.*, 1863, cxix., 56), Delafontaine (*Liebig's Ann. Chem.*, 1864, cxxii., 100), Bakhuys-Roozebooms, Urbain, Jannasch, Brauner, Kosmann, Chavastelon, Muthmann, Locke, Dennis, Matignon, Böttinger, Moissan, and many others (vide the excellent "Index to the Literature of Thorium," Jöuet, Smithsonian Miscellaneous Collections, No. 1374), yet the anomalous conduct of certain of its compounds has caused serious questions by several investigators as to its elementary nature.

Chroustchoff reported an element associated with thorium in certain zircons and American monazite sands (*Journ. Russ. Phys. Chem. Ges.*, xxix., 206; *Chem. Zeit.*, 1890). Although little information is to be had as to this work, apparently the atomic weight, 220, was attributed to the element, which was detected spectroscopically. As Crookes remarks, "the spectrum of thorium is even more complicated than that of iron"; hence, further data are necessary. Auer von Welsbach insists that thorium is complex

(*CHEMICAL NEWS*, lxxxv., 255; *Journ. für Gasbeleucht. u. Wasservers.*, 1901, p. 661).

In 1898, as adverted to, G. C. Schmidt (*Wiad. Ann.*, lxx., 141) and Madame Curie (Madame Curie's Thesis, *Faculté des Sciences de Paris*, 1903) independently noted the radio-activity of thorium obtained from Bohemian pitchblende. Not long after the announcement of the Becquerel rays (*Comptes Rendus*, 1896, cxxii., 420, 501, 559, 689, 762, 1086), Crookes showed that by fractionating uranium nitrate with ether, compounds could be obtained which did not affect the photographic plate (*Proc. Roy. Soc.*, 1900, lxxi., 406). This indicated the separation of a new substance (Uranium X), and that radio-activity was not an inherent property of the element uranium as maintained by Madame Curie (*Comptes Rendus*, cxxvii., 175).

Soddy and Rutherford (*Proc. Chem. Soc.*, xviii., 121) demonstrated that only material carrying the β -rays was thus separated, and that the so-called inactive (to the photographic plate) uranium still gave off α -rays which ionize gases, and may be detected by the electrical method. Crookes, in the same paper, reported a few preliminary experiments on thorium compounds, and suggested "the possibility of separating thorium from its radio-active substance" (*loc. cit.*).

In 1899 Debiere separated from pitchblende a strong active substance which appeared to consist of titanium (*Comptes Rendus*, cxxix., 593). On more accurate investigation, however, he proved it to be nearer akin to thorium, and having secured an oxide 5000 times as active as uranium, he named the element actinium (*Comptes Rendus*, 1900, cxx., 906).

Debiere gives some four methods for separating this element, to wit:—Precipitation of weak acid solution by sodium thiosulphate, treating the hydroxide with hydrofluoric acid and potassium fluoride, precipitation of the neutral nitrate by hydrogen dioxide, and precipitating lead or barium sulphate in the liquid, whereby the active body is carried down. While quantitative physical data, as atomic weight, specific gravity, spectrum, &c., are as yet not to be had, the qualitative conduct of the radio-active properties are fairly well defined.

Hofmann and Zerban examined a number of minerals from which thorium is obtained, and proved the presence therein of uranium (*Ber.*, 1902, xxxv., 531). The thorium oxides from all of these were radio-active. Norwegian gadolinite, orthite, and ytrotitanite free from uranium gave a thorium oxide which neither affected the electro-scope nor the photographic plate (*Ber.*, 1902, xxxv., 533 and 145). The radio-activity of actinium consists primarily of rays or "emanations" simultaneously discovered by Rutherford (*Phil. Mag.*, 1900, xlix., 2; 1903, [6], v., 95) and the Curies, in 1899 (*Rapports au Congrès Int. de Physique*, 1900, iii., 79). The gases emitted by radium and thorium are temporarily radio-active, and may be condensed at -150° and -120° respectively.

The work of Hofmann and Zerban, touching the primary activity of thorium, being questioned by Barker ("Radio-activity of Thorium Minerals," *Am. Journ. Sci.*, 1903, xvi., 164), is upheld by the junior author (Zerban, *Ber.*, 1903, xxxvi., 3911), who determined the presence of from 0.038 to 0.04 per cent of uranous oxide in monazite from Bahia and South Carolina. While the uranium obtained from this sand was quite radio-active, the thorium oxide discharged the electro-scope in two minutes and forty seconds, two minutes and forty-five seconds, and three minutes and five seconds (the instrument without radio-active substance three minutes and twenty-five seconds), and the β -activity affected the photographic plate in twenty-four hours. The reasons for this somewhat detailed account will shortly become apparent.

Brauner (*Proc. Chem. Soc.*, 1901, xvii., 67) reported that the heptahydrated thorium tetrammonium oxalate, which he has used in his excellent method for determining the atomic weight of that element (*Journ. Chem. Soc.*, 1898, lxxiii., 951), hydrolysed on diluting its water solution. By this means he obtained two constituents, which he design-

nated thorium α and thorium β , and ascribed the atomic weights 220 and 260—280 respectively. No subsequent publication on the subject has come from the Prague laboratory so far. At the same time the writer independently reported the results of his observations, extending over some five years, which pointed toward the existence of a new element associated with thorium, and gave it the name *Carolinium* (*Journal. Am. Chem. Soc.*, xxiii., 761). Since that time I have reported in fragments a number of observations in abstract along the same line. They and others are digested in this communication.

While it is unnecessary to recapitulate my first work in the leading paper referred to, it was stated that carolinium was found to be more radio-active than the original thorium. The statement was true for the body in the degree of purity had at that time when examined by the photographic, as reported, and later verified by the electrical method.* On page 761 (*loc. cit.*) it was stated:—"I am not yet ready to assert that the new substance obtained is not the third radio-active body reported by Debierne in pitchblende, actinium, which he states belongs to the iron group." From what follows it is apparent that carolinium and actinium cannot be the same. In fact, the former has little to do with radio-activity, which is the *raison d'être* for the latter.

The elegant researches of Rutherford and Soddy (*Proc. Chem. Soc.*, 1902, xviii., 2) prove that there can be no doubt of the existence of a novel highly radio-active substance with thorium (Thorium X), as it is usually extracted from minerals without consideration of their chemical composition, to which Hofmann and Zerban strenuously direct attention. Such prepared so-called pure salts of thorium contain a radio-active constituent, which may be concentrated chemically by precipitation with ammonia (the filtrate carries Thorium X), and washing the oxide with acid or even water (Rutherford and Soddy, *Phil. Mag.*, 1902, p. 370). The residues obtained by evaporation of the ammoniacal solution in the first case are a thousand times as active as the original, and "are free from thorium, or at most contain only the merest traces, and when re-dissolved in nitric acid do not appear to give any characteristic reaction" (p. 376). Again, the residue from the water washings became 1800 times as active, and after conversion into sulphate, Rutherford and Soddy state:—"No other substance than thorium could be detected by chemical analysis,"† although, of course, the quantity was too small for a minute examination."

Having this in mind, the writer requested Dr. H. S. Miner, chemist to the Welsbach Lighting Company, to save certain ammoniacal washings obtained in the process for the extraction and purification of thorium oxide from monazite sand for the manufacture of the Welsbach gas mantles. The ignited residue obtained from evaporating over 100 litres of this liquor produced a marked effect upon the photographic plate, and showed nearly three times the radio-activity of thorium by the electrical method, using the apparatus of Dolezalek. The radio-activity remained constant through a number of months. The body gave none of the chemical reactions, and did not show a single line of thorium in the arc spectrum made with a large Rowland grating.‡ Dr. Miner is securing an abundance of this material for us, and as soon as practicable this will be thoroughly investigated in our laboratory.

The writer, working with Lichtenhaler,§ has obtained highly radio-active bodies, tested by the photographic method, from thorium, cerium, didymium oxides, and the residual phosphates extracted by ourselves from North Carolina monazite sands. Further, we obtained an extremely active body by precipitating the sulphate solution with hydrogen sulphide, which perhaps would, but not

necessarily, indicate the presence of polonium according to the Curies (*Comptes Rendus*, 1898, cxxvii., 175).

When we consider that barium chloride containing radium may be precipitated by sulphuric acid or silver nitrate, and the filtrate or precipitate obtained thereby, supposedly containing none of that remarkable body, is still radio-active,* we can easily understand how in a mineral or salt a radio-active body, perhaps resembling one of the constituents, clings to various components throughout many chemical manipulations. It having been suggested that uranium might owe its radio-active properties to the presence of small amounts of polonium or radium, Mme. Curie (*Revue Générale des Sciences*, Jan., 1899; M. and Mme. Curie, *Comptes Rendus*, cxxvii., 175) states that such could not be true, and adds, in another paper (M. and Mme. Curie and M. Bémont, *Comptes Rendus*, cxxvii., 1215):—"The property of emitting rays . . . which act on photographic plates is a specific property of uranium and thorium. The physical condition of the metal seems to be of an altogether secondary importance. Uranium and thorium alone are practically active."

It is very foreign from the intention of the writer to be hypercritical of work which stands out so brilliantly, and will remain so for a long time to come, but very painstaking investigations have caused him to face about in this matter, not an unusual condition for scientific truth seekers. The power possessed by the thorium, as usually prepared, of inducing activity, reported by Rutherford and his co-workers (*loc. cit.*), is deeply interesting and supports our thesis. The brilliant French woman states, concerning uranium (*loc. cit.*):—"I have never found any marked difference between the relative activities of the same compound." By analogy one may consistently assume the same for thorium. We have obtained similar compounds of thorium fractions which do differ in their radio-activity, in some cases one being three times as great.

(To be continued).

ON THE DENSITY OF NITROUS OXIDE.†

By Lord RAYLEIGH, O.M., F.R.S.

In the *Proceedings*, 1897, vol. lxii., p. 204 (or "Scientific Papers," vol. iv., p. 350), I have given particulars of weighings of nitrous oxide purified by two distinct methods. In the first procedure, solution in water was employed as a means of separating less soluble impurities, and the result was 3.6356 grms. In the second method a process of fractional distillation was employed. Gas drawn from the liquid so prepared gave 3.6362. These numbers may be taken to represent the corrected weight of the gas which fills the globe at 0° C. and at the pressure of the gauge (at 15"), and they correspond to 2.6276 for oxygen.

Inasmuch as nitrous oxide is heavier than the impurities likely to be contained in it, the second number was the more probable. But as I thought that the first method should also have given a good result, I contented myself with the mean of the two methods, viz., 3.6359, from which I calculated that referred to air (free from H₂O and CO₂) as unity, the density of nitrous oxide was 1.52951.

The corresponding density found by M. Leduc is 1.5301, appreciably higher than mine; and M. Leduc argues that the gas weighed by me must still have contained one or two thousandths of nitrogen ("Recherches sur les Gaz," Paris, 1898). According to him, the weight of the gas contained in my globe should be 3.6374, or 1.5 milligrms. above the mean of the two methods.

Wishing, if possible, to resolve the question thus raised, I have lately resumed these researches, purifying the nitrous oxide with the aid of liquid air kindly placed at my

* This was kindly determined by Dr. Geo. B. Pegram, of the Physics Department of Columbia University.

† Italics theirs.

‡ By Dr. W. J. Humphreys, of the Broadway Rouss Physical Laboratory, University of Virginia.

§ Thesis for degree of Master of Science, unpublished.

* See the works of the Curies, Geisel, Elster and Geitel, Markwald, and others.

† A Paper read before the Royal Society, September, 1904.

disposal by Sir J. Dewar, but I have not succeeded in raising the weight of my gas by more than a fraction of the discrepancy (1·5 milligrams). I have experimented with gas carefully prepared in the laboratory from nitrate of ammonia, but as most of the work related to material specially supplied in an iron bottle, I will limit myself to it.

There are two ways in which the gas may be drawn from the supply. When the valve is upwards, the supply comes from the vaporous portion within the bottle, but when the valve is downwards, from the liquid portion. The latter is the more free from relatively volatile impurities, and accordingly gives the higher weight, and the difference between the two affords an indication of the amount of impurity present. After treatment with caustic alkali and sulphuric acid, the gas is conducted through a tap, which is closed when it is desired to make a vacuum over the frozen mass, and thence over phosphoric anhydride to the globe. For the details of apparatus, &c., reference must be made to former papers. The condensing chamber, which can be immersed in liquid air, is in the form of a vertical tube 2½ c.m. in diameter and 22 c.m. long, closed below and above, connected laterally to the main channel.

The first experiment on July 13 was upon gas from the top of the bottle as supplied, and without treatment by liquid air, with the view of finding out the worst. The weight was 3·605, about 35 milligrams too light. The stock of material was then purified, much as in 1896. For this purpose the bottle was cooled in ice and salt,* and allowed during about one hour to blow off half its contents, being subjected to violent shaking at frequent intervals. Subsequently three weighings were carried out with gas drawn from the bottom, but without treatment by liquid air. The results stand:—

July 18	3·6368
July 20	3·6360
July 25	3·6362
Mean	3·63633

Next followed experiments in which gas, still drawn from the bottom of the bottle, was further purified by condensation with liquid air. The gas, arriving in a regular stream, was solidified in the condensing chamber. When it was judged that a sufficiency had been collected, the tap behind was turned and a high vacuum established over the solid mass with the aid of the Töpler pump. The pump would then be cut off, and the gas allowed to evaporate and accumulate in the globe. A re-application of liquid air caused the gas to desert the globe for the condensing chamber, until in a surprisingly short time a vacuum was re-established. Little or nothing could now be drawn off by the pump, and it was thought that a distinct difference could be perceived between the first and second operations, indicating that in the first condensation a little impurity remained gaseous. If desired, the condensation could be repeated a third time. On one occasion (August 7) the condensed gas was allowed to liquefy, for which purpose the pressure must rise to not far short of atmospheric, and to blow off part of its contents:—

August 1	3·6363
August 3	3·6367
August 7	3·6366
Mean	3·63653

The treatment with liquid air raised the weight by only 0·2 milligram., but the improvement is probably real. That the stock in the bottle still contained appreciable impurity is indicated by a weighing on August 13, in which without liquid air the gas was drawn from the top of the bottle. There appeared—

August 13	3·6354
-------------------	--------

about 1 milligram. short of the proper weight.

* The lower the temperature below the critical-point, the more effective is this procedure likely to be.

It will be seen that the result without liquid air is almost identical with that found by the same method in 1896, and that the further purification by means of liquid air raises the weight only to 3·6365. I find it difficult to believe that so purified the gas still contains appreciable quantities of nitrogen.

The corresponding weight of air being 2·3772 (*Proc. Roy. Soc.*, 1893, vol. liii., p. 134; "Scientific Papers," vol. iv., p. 47), we find that, referred to air as unity, the density of nitrous oxide is—

$$\frac{3·6365}{2·3772} = 1·5297.$$

Again, if oxygen be taken as 16, the density of nitrous oxide will be—

$$\frac{3·6365 \times 16}{2·6276} = 22·143.$$

The excess above 22 is doubtless principally due to the departure of nitrous oxide from Boyle's law between atmospheric pressure and a condition of great rarefaction. I hope shortly to be in a position to apply the connection which will allow us to infer what is the ratio of molecular weights according to Avogadro's rule.

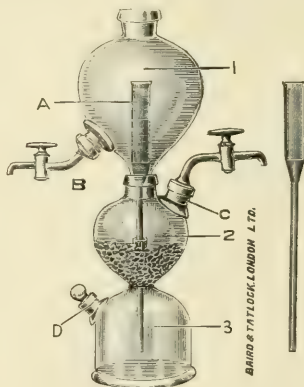
AN IMPROVED FORM OF KIPP'S APPARATUS.

By R. J. FRISWELL, F.I.C., F.C.S.

EVERYONE who has to work with the above well-known apparatus has had occasion to notice its many defects. Among these the most serious are:—

- (1) Rapid degeneration of the acid liquids and early appearance of sluggishness in the reaction.
- (2) Wastefulness of the acids.
- (3) Necessity for frequent re-charging, which, apart from the waste involved, is an unpleasant operation.

Having occasion to make constant use of several Kipp's for some months past, I was led to study the apparatus with the object of improving it, if possible, in these directions, and as a result have devised the modification here described, in which all the above objections are reduced to a minimum, and, in fact, practically abolished.



The form of the new apparatus is shown in the accompanying drawing.

1, 2, and 3 are the usual three bulbs of the ordinary Kipp's apparatus. At A in bulb 1 is shown the upper end of a tube ground in to the neck and passing down to the

bottom of the lowest bulb. This tube is very slightly flared at the top, which should be situate at about three-fourths of the diameter of the bulb from its lowest part. The bulb *r* is separate from the remainder of the apparatus, being ground in to the neck of bulb 2 as usual.

a is a neck with cock and tube serving to draw off contents of bulb 1. *c* is the usual neck and cock for outlet of gas from bulb 2. *d* is the neck with ground stopper in bulb 3; (with this form of apparatus this is not really necessary).

The tube *a* is shown in full outside the apparatus on the right hand side.

Before use the tube *a* must be securely fastened into its seating in the uppermost bulb 1. To do this gently warm the ground part of the tube at *e*, and of the bulb, smear on to the ground part of the tube a very little good fresh marine glue. Put it into its place and firmly press it home with a turning movement. Be careful that none of the marine glue gets on to the outer ground neck of bulb 1.

The apparatus may now be put together.

To use it charge the centre bulb 2 with the marble, zinc, or ferrous sulphide as usual, taking care that the material is free from dust. N.B.—A light layer of asbestos or glass-wool round the tube before putting in the material is advantageous if small fragments are to be used.

Now pour down the centre tube, by means of a funnel, sufficient strong calcium chloride, zinc sulphate, or ferrous chloride solution to fill up the lowest bulb nearly to the top. A space of half an inch between the top of this liquid and the lowest fragments in the centre bulb should be left at the least.

Now pour in the acid until the uppermost bulb is so filled that the acid stands an inch or so above the flared lip of the standing tube *a*.

It is, of course, necessary that all the cocks should be closed and the stoppers secured in their places.

The apparatus is now ready for work.

The following is the method of use:—Open the gas-cock slightly so as to allow the acid to descend very slowly. If the glass-cock works stiffly it is better not to depend on it, but to slip a rubber tube with a screw pinch-cock over the nose of the glass-cock. Close the pinch-cock, open the glass-cock, and then slowly open the screw pinch-cock.

If these directions are accurately followed the acid will descend the centre tube, and, rising through and floating on the strong salt solution in the bottom of the apparatus, reach the centre bulb at nearly full strength, and when the gas pressure rises the exhausted liquor will be slowly and steadily pressed back to the upper reservoir.

When the gas-cock is closed this action will be very noticeable. The liquids having changed places, the strong salt solution forced back to replace the acid will be seen falling over the lip of the flared tube in the upper reservoir through the stronger acid therein.

When an accumulation of this denser liquid in the upper reservoir takes place to such an extent that its level approaches the upper part of the standing tube, it can be drawn off by the cock *b*, and fresh acid carefully poured in by means of a funnel whose tube is long enough to enter about half an inch into the standing tube *a*.

If these instructions are carefully followed, the contents of the lowest part of the apparatus need never be disturbed or removed.

When the gas generating material in the centre is exhausted, or needs renewal, draw off from the cock *b* till the liquid is below the lip of the standing tube *a*; now insert a long stemmed 50 or 100 c.c. pipette into the standing tube and draw out its contents for 5 or 6 inches of its length, or to about the middle of the centre bulb 2.

The gas-cock and tube of this may now be removed, the new material put in, cock and tube replaced, upper reservoir re-charged with acid, and the apparatus at regular work in the course of a few minutes.

It is, perhaps, needless to point out that, as the economical action depends on the different densities of the fresh and the exhausted acids, a permanent place

should be found in the laboratory for the apparatus, which should be moved as little as possible, so as not to shake up and mix the strata of liquors in the upper reservoir.

In this respect it requires to be treated in exactly the opposite way to the old form of Kipp, in which, as the liquids were returned to the reservoir in the order of their entry into the gas generator, the liquid reaching the gas generating materials is always that most saturated, the freshest acid lying on the top, and requiring the liquid in the upper bulb to be well swung round in order to strengthen the exhausted liquor in the lower part of it, otherwise sluggish action is even sooner manifested than it would otherwise be.

As an example of the separation of the strengths, the following experiment may be given:—

The apparatus charged with exhausted liquor at the bottom and fresh acid in top bulb. The gas was shut off after some time, and a considerable quantity of the exhausted liquor forced up the tube *a*, and was seen to fall down through the acid in No. 1. A sample was drawn off; its gravity was 1.333, free HCl 6.86 grms. per litre. Some liquor was now drawn from just below the surface of the liquid in bulb No. 1 with a pipette. Its gravity was 1.276, and the HCl was found to be 26.02 grms. per litre.

It is, perhaps, needless to point out that scraps of marble, &c., must on no account be allowed to fall into the lowest bulb, or the effervescence will mix the strata therein.

MESOXALIC SEMIALDEHYDE.*

By HENRY J. HORSTMAN FENTON, F.R.S.

MESOXALIC semialdehyde ($\text{COOH}-\text{CO}-\text{CHO}$), it has been previously shown (Fenton and Ryffel, *Trans. Chem. Soc.*, 1902), can be obtained by the oxidation of dihydroxymaleic acid with ferric salts at about 40° . This method is not altogether satisfactory, owing to the difficulty of removing the iron salts, and it is now found that the oxidation may advantageously be effected by means of mercuric chloride. In this case the mercury separates almost quantitatively as calomel, and any traces remaining may be removed by hydrogen sulphide. The properties of this semialdehyde are being further studied, and appear to be of considerable interest. It is evident that the aldehyde hydrate, $\text{COOH}-\text{CO}-\text{CH}(\text{OH})_2$, may be regarded as a tautomeric form of the missing trihydroxyacrylic acid, $\text{COOH}-\text{C}(\text{OH})=\text{C}(\text{OH})_2$, and the latter should, by condensation with two molecules of urea, yield uric acid.

If a solution of mesoxalic semialdehyde is mixed with urea and heated, together with dilute hydrochloric acid, a large yield of a very sparingly soluble crystalline substance is obtained which, by its properties and composition, proves to be *glycoluril*, $\text{C}_4\text{H}_6\text{N}_4\text{O}_2$. This compound was originally obtained by reduction of allantoin, and afterwards from glyoxal and urea.

It is evident, therefore, that a molecule of carbon dioxide splits off in the reaction above described; later experiments appear to indicate, however, that by modifying the conditions this loss may be prevented, in which case it is hoped that uric acid itself may be obtained.

Although the properties of glycoluril have been carefully studied by various authors, the following very striking colour-reaction appears to have been overlooked:—The substance is evaporated to dryness with strong nitric acid on a water-bath, and the white residue dissolved in caustic soda; a faint blue violet colour here results, and now, on addition of sodium hypochlorite, a very brilliant purple colour is obtained.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

SOME OBSERVATIONS

ON THE GROUPING OF THE LINES IN THE SPECTRUM OF SILICON THROUGH THE EFFECT OF SELF-INDUCTION, AND THEIR PRESENCE IN STELLAR SPECTRA.*

By M. le Comte A. DE GRAMONT, D.Sc.

In a short note† presented to the meeting of the British Association at Southampton (1903) I gave the first results of my research on the comparison of the lines of silicon which, under the action of self-induction, remain or disappear, and the corresponding lines in stellar spectra. After having photographed the entire spectrum as far as λ 2930 with a spectrograph in which the optical system was entirely of quartz, and having repeated the middle portion with an Iceland spar prism, I made a special examination of the portion susceptible of astronomical comparison (given herewith) by means of two prisms of heavy flint glass and with an achromatic objective of 45 c.m. focal length. The negatives obtained had on their upper portions the ordinary condensed spark spectrum of silicon, obtained by means of a coil giving a 15 c.m. spark and a condenser of 0.005 microfarads capacity. In coincidence with this spectrum were photographed, one under the other, the spectra which resulted from the action of self-induction varying from 0.0002 to 0.03 henry. The wave-lengths were measured by comparison with those of a lead-cadmium alloy, and calculated by large scale curves or by means of an interpolation formula.

I would add here to my note of last year the results I have obtained since, and their comparison with the grouping Sir Norman Lockyer submitted the same lines to, by arranging them according to temperatures supposed to be increasing, in which Group IV. would correspond to the maximum temperature:—

Thermic groups according to Lockyer.	Groups classified according to the effect of self-induction.	
IV. { 4089.1 4096.9 4116.4	{ (O?) 4089.3 (N?) 4097.3 (N?) 4116.5 (N?) 4103.5	{ Disappear with a very slight self-induction (0.00008 H.) at the same time as the air spectrum.
III. { 4552.8 4568.0 4574.9	{ δ { 4552.3 4597.5 4574.6 3807.5 3796.0 3791.5 3794.5 3087.2 4131.0 4128.2	{ Become much weaker with the above self-induction, and disappear with a mean self-induction of 0.0006 H.
II. { 4131.1 4128.1 5042.0 5057.0 3853.9 3856.1 3862.7 3905.8 4103.2	{ ϵ { 3854.2 3856.1 3862.5 3905.7 γ { 5044.0 5058.7	{ The latter disappear with a self-induction of 0.006 H. { Resist the action of maximum self-induction, 0.03 H.

The lines of Group IV., which, according to Lockyer, indicate an excessive temperature, have, on my plates, always accompanied the air lines, and disappear with them. The lines coincide with the lines of oxygen and nitrogen, the presence of which has been detected in several stars in Orion and in θ Crucis (MacClean, "Spectra of Southern Stars," 1898). Therefore I am of the opinion that Group IV. does not belong to silicon. The line 4103.5

* Read before the British Association (Section B), Cambridge Meeting, 1904.

† To correct a misprint for a yellow line, in place of β 3879 read β 5079; compare with my previous work on silicon (*Comptes Rendus*, January 25, 1897).

does not appear to me to correspond with the line, 4103.1, found by Rowland in the arc spectrum of silicon and in the ordinary solar spectrum (but not at all in the spectrum of an eclipse); I believe it, also, is due to air.

Group III. might be completed by the triplet, Si η , which accompanies Si δ in ϵ *Canis majoris* and in several stars in Orion. The doublet Si θ will be detected perhaps some day with a reflector and a quartz prism. The two green lines, Si γ , should not be included in this group, as they absolutely resist the strongest self-induction I have been able to use; they might be considered as low temperature lines, and be placed in Group I. with the line Si ζ , 3905.7, common to the arc and the spark, and which belongs to the ordinary solar-spectrum, as well as to the "flash-spectrum" of eclipses (Evershed).

The triplet ζ_2 and the doublet ϵ in the violet appear to be closely associated and concomitant in the spectra of stars, as well as in regard to self-induction; thus they remain in the same group.

From what has preceded, and considering, on the one hand, the lines that are made successively to disappear by self-induction from the spark spectrum, and on the other hand the distribution of the corresponding lines in stellar spectra, we may draw the following conclusions:—

1. Only the stars of Secchi's first class, those containing hydrogen and helium, show the lines of silicon suppressed by self-induction, the properly called helium stars, like those in Orion or ϵ *Canis majoris*, show the lines Si δ , Si η very strongly, and they disappear the first. The more specially hydrogen stars like Sirius, and those which approach the solar type, like Procyon, show more particularly the lines Si ϵ and Si ζ_2 ; the latter disappear on increasing the self-induction.

Deneb (α Cygni), which appears to be in an intermediate stage, shows simultaneously the characteristic lines of both these categories of stars.

2. The stars of the second class (solar type) showing the special lines of the arc, comprise Si ζ , common to the arc and the spark. It would be interesting to try whether some of the stars of this class would not also give the persistent doublets Si α in the red (6320—6342) and Si γ in the green. These two latter doublets, Si α and Si γ , are the most distinct and the most sensitive for analytical chemistry.

3. The stars with band spectra, the third and fourth classes, with not very high temperatures, have not yet shown any silicon lines.

Thus we see that the distribution of the silicon lines in the stars appears to be in accordance with the usual classification of these latter.

In the most refrangible portion of the spectrum, and with no astronomical correspondence, the strong line 2542 disappears with a self-induction of about 0.006 H. The other lines, especially the very characteristic group of six lines (2529 to 2507), having an extreme sensitiveness in regard to chemical analysis as pointed out by Mr. Hartley (*Proc. Roy. Soc.*, March 25, 1901), in the case of solutions, and the group 2217 to 2209, resist the maximum self-induction of 0.03 H without apparent diminution. Finally, I have found that the extreme line 1930.0 does not belong to silicon but to aluminium. In this research I have made use of silicon crystallised in small octahedra, and in plates; also silicate of sodium fused in the blowpipe on platinum wires. As I have already shown, the effects of self-induction are the same with solid bodies and with fused salts submitted to the action of the spark.

NOTE.—In 1895, the CHEMICAL NEWS (vol. lxxii., p. 103) contained the summary of a paper by M. de Gramont presented to the Académie des Sciences, Paris, on the "Direct Spectral Analysis of Minerals." The paper which appeared in our last issue (p. 140) is a continuation of this work.

ERRATA.—P. 140, col. 2, line 18 from bottom, for "scale" read "grating." Last line of Table, col. 2, for "3495.4" read "3497.4."

ON THE BEARING OF THE
COLOUR PHENOMENA PRESENTED BY
RADIUM COMPOUNDS.*

By WILLIAM ACKROYD.

MADAME CURIE early observed that radium salts are white like barium salts when first prepared, but that they gradually become coloured ("Thesis on Radio-active Substances," p. 30; London, CHEMICAL NEWS Office). I have associated this colour-change with the reception of external radiant energy and the consequent increase of radio-activity (*Lancet*, November 21, 1903, p. 1464). What I take to be confirmation of this view has been obtained in following the history of a radium bromide tube. The salt was nearly white when purchased, and in a month or two it became tawny-yellow or orange; its powers of absorption had visibly increased, and its power of exciting fluorescence in barium platino-cyanide was concurrently quadrupled. These facts may be thus diagrammatically represented:—

Colour-change and increase of absorption.

White, yellow, orange, tawny-orange.

Increase of radio-activity.

This readiness on the part of radium compounds to become coloured under the influence of external radiations may be regarded as an effort to conform to the constitutive-colour law (*B.A. Report*, 1903, and *CHEMICAL NEWS*, 1903, lxxxviii., 217); moreover, it is highly probable that the colour-change is effected by a minimum expenditure of energy, as in the case of other end members of vertical groups of the periodic classification of the elements. This tendency I have experimentally demonstrated in the case of chlorides of alkali metals (*Journ. Chem. Soc.*, 1904, lxxxv., 815).

But while we may regard this colour-change as being slowly effected by external radiations, the comparatively sudden application of sensible heat has a very different effect. In July, 1903, I strongly heated tawny-orange radium bromide, expecting to see it change in this order—red, brown, black, like mercuric oxide and other colour-changing bodies. Instead, the seething substance reverted at once to white. The colour behaviour of the radium bromide when heated is evidently anomalous like some other compounds of extreme members of vertical periodic groups; as, for example, mercuric iodide. Its powers of absorption are visibly lessened, and, as is now well known, the radio-active properties of the residue are also lessened. The increase in the radio-activity of the expelled emanation is another phenomenon, and probably the joint product of radium rays and heat. Analogous effects are produced by radium rays and heat on halides of the alkali metals (*Journ. Chem. Soc.*, 1904, lxxxv., 816). Cesium chloride was exposed to radium rays for half-an-hour at 16° C.; the radium compound was then removed, and the temperature of the cesium salt was raised to 37° C. The phosphorescence was now markedly increased by the rise of temperature. May we not, then, suppose that the bodies occluded in radium compounds have radio-activity conferred on them while there, and that this radio-activity is increased by the heat which is necessary for their expulsion?

Crucial tests of the validity of this energy-transformation theory appear to be presented in the following additional facts. If water be admitted to the contents of a radium bromide tube its phosphorescence is practically undiminished (*CHEMICAL NEWS*, 1903, lxxxviii., 206). Rutherford has studied the matter quantitatively, and finds that solution of a solid radium compound to a thousand times its volume does not appreciably affect its radio-activity, which he has attempted to explain on the atomic disintegration theory

(*Nature*, 1904, lxxx., 222). I have, however, pointed out that under such conditions there is approximate constancy of absorption of external radiant energy which ought to result in a like constancy of radio-activity (*Nature*, 1904, lxxx., 295).

Again, the 60 per cent difference of heat emission in the Curie-Laborde and Curie-Dewar estimations appears to receive a rational explanation from this point of view. At normal temperature the output of heat from a radium compound was found to be of the order of 100 calories per gm. of radium per hour, while at the temperature of boiling oxygen it was only 38 calories. Now a colour-changing substance, whilst passing from normal temperature towards the region of absolute zero, becomes white, or, in other words, lessens its capability of absorbing external radiant energy; and it is now suggested that probably to this cause is to be attributed the low numbers obtained by Professors Curie and Sir J. Dewar at the temperature of boiling oxygen.

A CONTRIBUTION TO THE THEORIES OF
OSMOSIS, SOLUBILITY, AND NARCOSIS.*

By Professor I. TRAUBE, Berlin.

UPON the results of a series of investigations, by plasmolytic methods, of the velocity of the osmosis of chemical compounds into the protoplast, Overton bases the theory that the magnitude of the distribution coefficient between such substances as fat, cholesterolins, and lecithins on the one hand, and water on the other, determines the velocity of the osmosis. He assumes that, in the first instance, a dissolution takes place in the fatty substance of the membrane at a velocity proportional to this coefficient, and that thereupon the substance passes on from the membrane to the interior of the cell. Moreover, Overton, and, independently, Hans Meyer, point out that all the reliable narcotics, anesthetics, and antipyretics belong to the class of rapidly diffusing substances, and hence they deduce the theory that the efficacy of a narcotic depends principally on its lipid solubility. These theories, however, in so far as they concern osmotic velocity, are erroneous. The author's investigations on the constants of capillarity of substances, especially solutions, have led to the result that the greater the osmotic velocity of a substance soluble in water the more this substance reduces the constant of capillarity of water, whilst substances which cannot penetrate membranes (with regard to which the membranes are impermeable) raise this constant. Among hundreds of compounds examined plasmolytically by Overton, and as to capillarity by the author, there is not one case in which capillary and osmotic phenomena do not correspond. It is evident that osmotic velocity and surface tension run parallel. Hence the difference of the surface tensions—or of the internal pressures—is the motive force in osmotic phenomena; it is to this difference that osmotic pressure is due.

The theory here stated leads to a new conception of the phenomena of diffusion and solution. Suppose that an aqueous solution of a salt be brought in contact with pure water. According to the prevalent theory the salt particles or the ions, in virtue of their "osmotic pressure," migrate into the pure solvent; but according to the author's view it is the pure solvent which, in virtue of its low surface tension, migrates into the salt solution. Again, let two liquids capable of dissolving in each other be brought in contact, or let a solid be in contact with a pure solvent, then the solution tension will depend chiefly on the difference between the surface tensions. From this we may expect that when a liquid or a solid substance dissolves in a solvent, the surface tension of the solution will never fall below that of the dissolving substance, and if the surface

* Read before the British Association (Section B), Cambridge Meeting, 1904.

* Abstract of a Paper read before the British Association, Section B, Cambridge Meeting, 1904.

tensions of solution and dissolving substance be equal, the solution will be saturated. The surface tension of a saturated solution is *in maximo* as low as that of the dissolved substance; consequently, the latter value determines the shape of the curve of the surface tension of solutions.

From the author's former investigations he deduced the law that equal equivalents of substances belonging to homologous series, which exercise a strong influence on capillarity (ordinary alcohols, fatty acids, esters, &c.), lower the capillary height of water in the proportion $1:3:3^2:3^3$ If 3 molecules of methyl alcohol reduce the surface tension of water as much as 1 molecule of ethyl alcohol, the conclusion is justified that the tendency to enlarge the surface of water is three times less in the case of methyl alcohol than in the case of its nearest homologue. Hence the tendency of methyl alcohol to separate from the solution may be considered as three times less than the corresponding tendency of ethyl alcohol; or, in other words, the solution tension of substances belonging to homologous series, which exercise a strong influence on capillarity, increases with increasing molecular weight in the proportion $1:3:3^2:3^3$

If a layer of a liquid insoluble in water, say, benzene, be placed upon an aqueous solution of different alcohols, esters, &c., the amount of dissolved substance of which this liquid will deprive the water will be greater in exact proportion as the solution tension is less. Distribution coefficients and solution tension—are therefore proportional magnitudes in first approximation.

Thus Overton's theory is erroneous in so far as it represents penetration into the cell as depending on the degree of lipid solubility; for dissolution of the dissolved substance in the lipids certainly does not take place. The motive force is the surface tension. Overton and Meyer have pointed out that the efficacious narcotics, anaesthetics, and antipyretics all belong to those compounds which penetrate thin membranes rapidly. Rapid penetration into the cell seems to be the most essential condition for enabling a narcotic to exercise its effect on the interior of certain cells. Thus narcotics which differ materially in their chemical composition may possibly exercise their action in different cells, and this action may vary considerably even when exerted on one and the same species of cell. But if narcotising substances of the same homologous series, such as the ordinary alcohols or esters, be considered, we are brought to the conclusions that the cells acted on are all of the same species, that the action in the interior of the cell only differs in degree, and finally that this difference depends essentially and solely on the velocity with which the homologous substances penetrate into the cells. Now this velocity has been shown to be proportional to the depression of the surface tension of water by the dissolved substances, and hence we cannot but conclude that the same law holds good for the narcotic action of homologous substances as has been proved to be valid for surface tension, and approximately so for the distribution coefficients.

ACTION OF H_2O_2 ON CARBOHYDRATES IN THE PRESENCE OF FERROUS SULPHATE.*

By R. S. MORRELL and A. E. BELLARS.

This investigation has been in progress for nearly six years in conjunction with Mr. J. M. Crofts, and lately with Mr. Bellars.

The production of dihydroxymaleic acid from tartaric acid by Fenton in 1894, showed that this oxidising agent exercised a peculiar action on secondary alcohol (CHOH) groupings. Cross and Bevan, in 1898, pointed out that

carbohydrates, which were unacted upon by hydrogen peroxide at the ordinary temperature, were very readily attacked if a little ferrous sulphate was added, and amongst the products was a substance which reacted strongly with phenylhydrazine at the ordinary temperature. By agreement with these three investigators, we have examined the oxidation products of a series of pentoses, hexoses, and bioses, and have found that the substance which reacts with phenylhydrazine at the ordinary temperature is of the nature of an osone. E. Fisher, in 1889, pointed out that osones are not fermented by yeast, and in our experiments, after fermenting off the sugar unacted upon by the hydrogen peroxide, the solution still reacts with phenylhydrazine at the ordinary temperature to give an osazone.

Glucosone has not been obtained crystalline, but only in the form of a syrup or amorphous solid. On reduction with zinc dust and acetic acid, it yields a levorotatory solution, which reacts with phenylhydrazine to give an osazone melting at 206° .

The yield of the osazone, obtainable at the ordinary temperature, depends upon the nature of the sugar. Fructose, glucose, mannose, and cane-sugar give the best yields.

Rhamnose is next in order; arabinose gives a small quantity only, while galactose does not yield a true osazone. Amongst the bioses, lactose gives none and maltose only a small amount, and the quantity does not seem less even after fermentation.

During the last year, investigations on the change in optical activity during the oxidation have been undertaken, and the results are of some interest. In the case of the hexoses, the fall in angle is fairly proportional to the amount of peroxide added up to 1 grm. molecule of H_2O_2 .

Glucose, fructose, and galactose were the hexoses examined. In the two former cases, the diminution in optical activity was practically the same, but in galactose the drop is much greater, and it was found that galactose gave a ketoacid of the hexose rather than an osone. The diminution in optical activity on oxidation in the case of the bioses seems to be connected with their tendency to be hydrolysed. Maltose shows the smallest drop in angle, and is hydrolysed with much greater difficulty than cane-sugar.

Lactose lies between maltose and cane-sugar, and this agrees with its power of being hydrolysed. Cane-sugar shows a drop in angle exactly the same as glucose and fructose.

Two pentoses have been investigated, arabinose and the methyl pentose rhamnose. Arabinose lies between glucose and galactose, but rhamnose shows an extraordinary behaviour; the original sugar is dextrorotatory, but on oxidation it becomes levorotatory, which is partly due to the osone, and partly to an acid which is not rhamnonic acid.

The acids formed are by no means easy to identify, for the yield of the lead salts is very small. The dibasic acid formed, which has been identified in the case of glucose, fructose, and rhamnose, is oxalic acid precipitated by normal lead acetate; the monobasic acids, which have been obtained from fructose and glucose by the use of four atoms of oxygen, are glyoxylic, glycollic, and trioxibutyric acids, but in addition there is, in the case of all the sugars investigated, evidence of a keto acid other than glyoxylic acid brought down partially by normal lead acetate, and completely by basic lead acetate.

In connection with the action of bases on the osones, it was found that an alcoholic solution of an osone reacted with guanidine to give a white semicrystalline substance, which contained 14.87 per cent $CN_2H_5 \cdot C_6H_{10}O_6(C_2H_5OH)$ requires 14.64. We have been unable to find any reference to guanidine compounds of sugars, and it was thought advisable to prepare a series of them and to investigate their properties. Glucose, fructose, galactose, arabinose, rhamnose, and maltose have been examined, and their compounds with guanidine have been investigated. These compounds, in the case of those with glucose and maltose,

* Read before the British Association (Section B), Cambridge Meeting, 1904.

are addition products of 3 molecules of the sugar with 2 of guanidine. In water they are strongly alkaline, and by dilute acids, N/10 HCl and oxalic acid, the guanidine is completely and quantitatively removed.

They are apparently not hydrolysed immediately by water, for their optical activity is much less than that of the parent sugar. In the case of glucose, the specific rotation $(\alpha)_D = +29.8^\circ$, and after five days has become $(\alpha)_D = -5.7^\circ$. An aqueous solution of the substance neutralised by HCl gave the rotation for free glucose. This behaviour is similar to that of sugars with alkalis referred to by Löbry de Bruyn.

A NEW THEORY OF THE PERIODIC LAW.*

By G. J. STOKES.

VARIOUS mathematical interpretations have been proposed of the Periodic Law. The following is not a mathematical but a logical interpretation of the law, and enables us to arrive at chemical results deductively. It is the chemical application of a more general method applicable to mathematics and physics.

It has been shown by De Morgan (*Cambridge Trans.*) that the relations between any two things x and y , if we take account not only of x and y but also of not- x and not- y , admit of seven, and only seven, varieties.

These relations were termed by him:—(1) Identical, (2) sub-identical, (3) super-identical, (4) complete particular, (5) super-contrary, (6) sub-contrary, (7) contrary.

The following diagrams taken from Mr. Keynes's "Formal Logic," Third Edition, illustrates these relations in the order given. The notation is slightly changed.

I have substituted, to express the negative, small letters instead of dots for the sake of clearness.

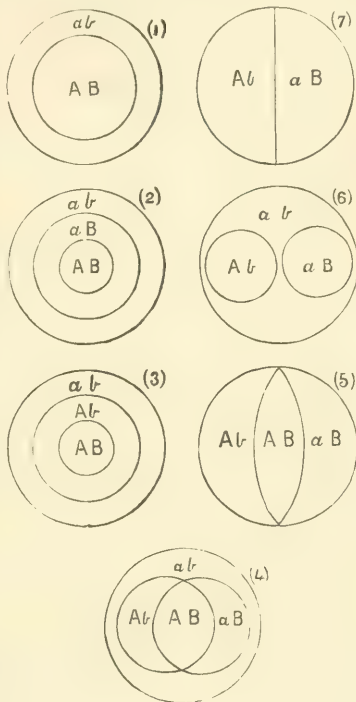
Shortly after the appearance of the Third Edition of Mr. Keynes's "Logic" in 1894, I applied these diagrams to the first seven elements arranged according to their order in the periodic classification: (1) representing Li, (2) Be, (3) B, (4) C, (5) N, (6) O, (7) F. I then, in accordance with a principle underlying the whole relation of logical forms to nature, considered the diagrams to combine in such a way that the large letters entered into combination with the small, so that in each case a pair of letters combine simultaneously. Each separate compartment of a diagram has an affinity for, and enters into, combination with that compartment, or those phases of two compartments of another diagram, or of its own diagram, which are most unlike. There results a scheme of arrangements conformable to and parallel with the chemical facts, so that these might have been predicted beforehand. It gives the forms of combination, the affinities, tells what bonds are satisfied, and how many left unsatisfied. It enables us to predict stability or instability of the compound, and sometimes physical features, such as hardness, *e.g.*, the diagram for carbon gives three forms, one of which, involving combination in every available way, I take to be the diamond.

I have endeavoured to extend it to succeeding series in the periodic arrangement of the elements. The conclusion I have reached is that the same principle applies to elements of higher atomic weight, that the difference is quantitative or numerical, and would involve duplication, triplication, &c., of the diagrams. They then become so complicated that they cannot be read easily. With regard to those groups falling into the eighth class of the elements, as Fe, Co, &c., I have not yet succeeded in finding a diagrammatic interpretation.

The form of diagrams given above, while useful in logic, are not those best adapted for physical investigations. I was therefore early led to try diagrams in tri-dimensional space. This of itself suggested the application to crystals.

If, as some crystallographers recognise, there are seven systems, this might help to explain the connection between chemical properties and crystalline form.

If the theory here put forward is true it may be asked in what direction does it point? At first sight it may appear opposed to the most recent ideas of physical chemistry.



It is impossible, however, not to recognise the close analogy between the positive and minus signs of the diagrams and positive and negative electricity. It is best to confine oneself to the most general and abstract statement, that the variety of the members of the periodic series depends on the varying relation of two principles towards each other, which are capable of every one of the relations of identity, exclusion, &c., which are logically possible between them.

NOTICES OF BOOKS.

Electro-chemistry. Part I. By R. A. LEHFELDT, D.Sc. London, New York, and Bombay: Longmans, Green, and Co. 1904.

THIS book, which is one of the series of text-books of physical chemistry edited by Sir William Ramsay, deals with the general theory of electro-chemistry, and includes a chapter on the "Relation of Chemical Constitution to Conductivity," written by T. S. Moore, B.A., B.Sc., which will be found of great interest by students of organic

* Read before the British Association (Section B), Cambridge Meeting, 1904.

chemistry, in which region new results of importance are being obtained almost every day by the application of electrical methods. This chapter, which is limited to the study of aqueous solutions, gives a very complete and succinct account of the subject. The rest of the book is divided into two chapters on the "Mechanism of Conduction in Electrolytes" and the "Theory of Chemi-electromotive Force" respectively. The first of these subjects is treated very fully, but the author does not succeed in making it interesting, so that the student will find a good deal of the chapter dull and troublesome reading. This is indeed the chief blemish on the whole book, though it is less to be remarked in the pages on chemi-electromotive force, which include a description of the construction, &c., of normal cells. The student who works through this book should have a very good knowledge of the chief facts and theories of electro-chemistry, but it seems hardly probable that he would be inspired with enthusiasm for the subject.

An Introduction to the Study of Spectrum Analysis. By W. MARSHALL WATTS, D.Sc. (Lond.), B.Sc. (Vict.), F.I.C. London, New York, and Bombay: Longmans, Green, and Co. 1904.

The author of this book has endeavoured to produce a work which shall be of service to the beginner, and at the same time give an account of the very latest developments of the subject, and these two aims have somewhat militated against one another. In accordance with the first, the most elementary optical principles and facts are described and explained very simply, even the trigonometrical ratios being defined, so that very few calls are made upon the readers' previous knowledge of elementary physics and mathematics. The chapters on the means adopted for the production of spectra are followed by freely illustrated descriptions of the spectra of stars and nebulae, and of the sun, the discovery of new stars, and the spectra of comets, and a discussion of the relationships between the lines of the spectra of allied elements and between the different lines of a spectrum, which is very lucidly treated. Thus the work will be seen to cover a fairly wide ground on the whole very successfully. It includes a catalogue of spectra, and in an appendix a paper by Sir William and Lady Huggins on the "Relative Behaviour of the H and K Lines of the Spectrum of Calcium," and a preliminary note by the same authors on "Some Modifications of the Magnesium Line at λ_{4481} under Different Laboratory Conditions of the Spark Discharge."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 7, August 16, 1904.

A Crystalline Compound of Lead Acetate and Lead Sulphate, $2\text{S}_2\text{O}_3\text{Pb}(\text{CH}_3\text{—CO}_2)_2\text{Pb}$.—P. Lemout. — When a dilute solution of sodium thiosulphate is added to a solution of lead acetate, a white precipitate of lead thiosulphate is formed. If acetic acid is then added, this precipitate disappears more or less completely according to the concentration of the original mixture. If the conditions are favourable for complete solution of the precipitate, and the whole left for a little time, a compound in the form of very heavy fine white needles separates out. These are sometimes 3 or 4 m.m. long. An analysis of this compound proves it to have the formula $2\text{S}_2\text{O}_3\text{Pb}(\text{CH}_3\text{—CO}_2)_2\text{Pb}$.

Alloys of Zinc and Magnesium.—O. Boudouard.—The author prepares the compound Zn_2Mg by acting on a

mixture of zinc and magnesium (80 per cent Zn to 20 per cent Mg) with a 0.3 per cent solution of hydrochloric acid. When left in contact for several days the metal disintegrates and gives a metallic powder, of which the composition corresponds to the compound Zn_2Mg . To isolate the compound ZnMg_4 , a mixture of zinc and magnesium (70 per cent Mg, 30 per cent Zn) is treated with a 0.5 per cent solution of ammonium hydrochlorate and heated for several hours. A metallic powder corresponding to the above formula is deposited. Without heat this latter reaction takes a very much longer time.

Constitution and Properties of Chromium Steels.—Léon Guillet.—The author examines by micrography and mechanical methods two series of chromium steels: one containing very little carbon and the other about 0.850 per cent of carbon. In each series the chromium increases from 0 to 40 per cent. His experiments lead him to subdivide chromium steels into four classes. From an industrial point of view, steels containing a double carbide should be rejected; they are too fragile. The martensitic steels, owing to their very great hardness, can only be employed in particular cases. Of all the martensites which the author examined, those containing chromium are the hardest. This fact explains the use of chromium steels for certain tools, such as files.

Evolution of Structure in Metals.—G. Cartaud.—The metals examined by the author are the most fusible, such as lead, tin, or zinc; his chief experiments as to the structure of the metal being performed on lead.

MISCELLANEOUS.

Photo-Engraving and Lithography.—We have much pleasure in drawing attention to the prospectus of the London County Council School of Photo-Engraving and Lithography (6, Bolt Court, Fleet Street, E.C.), the work of which is particularly identified with the printing craft. Principal: A. J. Newton. The Tenth Session will commence on Monday, September 26th. The School is open to those who are genuinely engaged in business in any branch of the photo-mechanical, photographic, designing, illustrative, lithographic, engraving, and printing crafts, and no provision whatever is made for amateurs. The courses of practical instruction are arranged to suit the following craftsmen:—

Photo-Engravers.—Line and screen negative making, etching, proving, tricolour work. Photogravure and preparation of originals for reproduction.

Photo-Lithographers.—Negative making, photo-lithography, colotype (plate preparation, press, and machine work), combinations of lithography and colotype.

Photographers.—Line and continuous tone negative making, printing, enlarging, transparency making.

Lithographers.—Lithography, map and plan drawing, transfer writing, drawing, design, lettering, photo-lithography.

Designers.—Design, drawing, lithography.

Draughtsmen.—Drawing, design, lettering. Pictorial composition.

The School is well equipped with the necessary appliances for study and practical work. It contains large studios for life and elementary drawing, design rooms, lithographic studio, lithographic press room, photographic studio with electric light installation, dark rooms, colotype preparation and printing room (with three presses), etching rooms, lecture room, &c. Only those engaged in the trade are admitted. The inclusive fees are:—Session of from thirty to forty weeks, 10s.; those in receipt of less than 30s. weekly, 4s. 6d. a Session. Trade apprentices, learners, and improvers (under 21) admitted free. The Photo-Process Department is open for day instruction. Further particulars will be found in the prospectus of the School.

The Preparation of Sulphamide.—O. Ruff.—The author saturates 400 grms. of chloroform with ammonia gas, and into the strongly cooled liquid he lets fall, drop by drop, a mixture of 100 grms. of chloride of sulphuryl and 100 grms. of CHCl_3 , taking care to stir well between each drop. This operation is stopped when all the ammonia is consumed (the drops then no longer react violently). The liquid is again saturated with ammonia, and the operations are repeated until all the SO_2Cl_2 is used up. Saturate again with ammonia, for the last time, and let stand in a well-stoppered bottle. A pasty mass is left floating on the chloroform; this latter will serve for a further operation. The pasty mass is dried in the oven at 100° (all traces of moisture must be guarded against in these operations), and ground in a warm mortar with warm sand; the whole is then exhausted with acetic ether free from water for four or six hours. The sulphamide then crystallises easily from this solvent, giving a return of 8 or 9 grms. It is fusible at 92° .—*Berichte*, vol. xxxvi., p. 2900.

Ponderable or Gasometric Estimation of Phosphoric Acid and Magnesia, Based on the Molybdenum Method.—E. Riegler.—I. *Ponderable Estimation of Phosphoric Acid.*—When we pour chloride of barium into an ammoniacal solution of phosphomolybdate of ammonia, the phosphoric acid is precipitated entirely in the form of phosphomolybdate of barium, $\text{Ba}_{27}(\text{MoO}_4)_{24}\text{P}_2\text{O}_8 + 24\text{H}_2\text{O}$. The considerable molecular weight of this precipitate enables us to estimate traces of phosphorus with accuracy, say, from 10 to 50 m.grms. of P_2O_5 , to within 0.1 m.grm. II. *Gasometric Estimation.*—Phosphomolybdate of barium is precipitated by a titrated solution of chloride of barium. We measure the excess of the reagent by means of the volume of nitrogen given off on the addition of iodic acid, and then sulphate of hydrazine. III. *Ponderable Estimation of Magnesia.*—Transform the ammonio-magnesian phosphate into phosphomolybdate of ammonia, then into the barium salt. IV. *Gasometric Estimation.*—This is effected in the same manner as that of the phosphorus. These two latter methods can be applied to the estimation of the magnesia in waters.—*Zeit. Anal. Chem.*, vol. xli., p. 675.

Electrolytic Reduction of Carbonic Acid.—Alfred Cohn and Stefan Jahn.—The authors found that it is impossible to reduce carbonic acid in acid solution, or carbonates by electrolytic methods, while it has long been known that nascent hydrogen readily reduces carbonic acid and the bicarbonates of the metals of the alkalis and alkaline earths to salts of formic acid. From these negative results they conclude that it cannot be either the undissociated molecule (in the case of CO_2) on which the hydrogen acts, or the CO_3 ion which is present in solutions of carbonates. On the other hand, they found that on electrolysis solutions of sodium bicarbonate the formation of reduction products could be readily proved by titration with permanganate; further experiments showed that the only product was formic acid; formaldehyde, oxalic acid, &c., not being formed. The reduction of bicarbonate shows that it is the HCO_3 ion which undergoes reduction. The electrolytic reduction of carbonic acid results when electrodes are used from which hydrogen is discharged at a high potential. The only product at all potentials at which reduction occurs is formic acid.—*Berichte*, xxxvii., No. 12.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving, and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Rock Sections.—What are the best authorities to consult on the study of rock sections and the apparatus, &c., necessary to prepare them?—H. T. FRENCH.

Alchemy.—Could any correspondent furnish me with a list of the more important works on alchemy and the alchemists extant, in English or French, with publisher and price if possible?—ALEX.

BATTERSEA POLYTECHNIC, S.W.

Principal—SIDNEY H. WELLS, Wh. Sc. A.M.I.C.E., A.M.I.E.E.
Head of Department—JOHN WILSON, M.Sc.

SESSION begins on MONDAY, SEPT. 26th.

DAY and EVENING CLASSES in ORGANIC and INORGANIC CHEMISTRY (Theoretical and Practical) up to Hons. B.Sc. (London).
SPECIAL COURSES in TECHNOLOGICAL CHEMISTRY, e.g. Paper Making, Paper and Pulp Testing, Gas Analysis, Assaying, Oils, Fats, Soaps, and Candles.
Complete courses of instruction (including Engineering subjects, German, Physics, &c.) for intending Works Chemists and General Analysts.
The Laboratories are open for Research.
Prospectus gratis on application to the SECRETARY.
Detained Prospectus 14, post free 3d.

BIRKBECK COLLEGE,

Breams Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

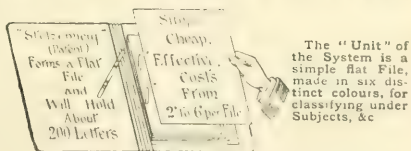
Courses for University of London, Conjoint Board, Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.

Perfect Order amongst your Scientific Papers, Research Records, &c.,

IS SECURED BY THE

“STOLZENBERG” SYSTEM of FILING.



Used by SIR WILLIAM CROOKES, LORD KELVIN, Royal Commission on Tuberculosis, Baden Aniline Works (50,000), and by thousands of private persons as well as Business Concerns.

Satisfaction guaranteed, otherwise goods taken back and money returned.

Sample Set, consisting of 12 best Files, 4to and fcap., with strong nickel-plated Perforator, and Patent Lifter, packed in leather-board box, 10/6 post free.

THE STOLZENBERG PATENT FILE CO.
50, Bishopsgate St. Without, London, E.C.

THE SIR JOHN CASS TECHNICAL INSTITUTE. JEWRY STREET, ALDGATE, E.C.

Principal—CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.

EVENING CLASSES IN CHEMISTRY, METALLURGY, PHYSICS, and MATHEMATICS.

Designed to meet the requirements of those engaged in CHEMICAL, METALLURGICAL, and ELECTRICAL INDUSTRIES, and in trades associated therewith.

Also preparation for the B.Sc. Examination of London University. Every facility for Special and Advanced Practical Work in well-equipped Laboratories, both in the Afternoon and Evening.

CHEMISTRY [CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.]
PHYSICS R. S. WILLOWS, D.Sc., M.A.
METALLURGY C. O. BANNISTER, Assoc.R.S.M.
MATHEMATICS G. M. K. LEGGETT, B.A.

CLASSES IN METALLURGY.

GENERAL METALLURGY.

THE METALLURGY OF GOLD, SILVER, and LEAD.

FUEL and REFRACTORIAL MATERIALS.

METALLOGRAPHY, including PYROMETRIC WORK.

ASSAYING.

ANALYTICAL CHEMISTRY.

Including ELECTROLYTIC and GAS ANALYSIS.

Each Course of Lectures will be accompanied by suitable Laboratory Work.

GLASS BLOWING.

A series of Courses of Instruction will be given during the Session by Mr. A. C. COSBOR.

New SESSION begins MONDAY, SEPT. 26th.

The Institute is readily accessible, and near to Fenchurch Street, Liverpool Street, Broad Street, and Metropolitan Railway Stations. For details of the Classes apply at the Office of the Institute, or by letter to the PRINCIPAL.

W. H. DAVISON, M.A.,
Clerk to the Governing Body.

THE POLYTECHNIC,

309, REGENT STREET, W.

UNIVERSITY OF LONDON PREPARATION CLASSES.

Full Courses of Instruction for Matriculation,

Inter. Arts, Science, and Engineering, and Final Arts.
Special Courses for Final B.Sc. in Mathematics, Physics, and Chemistry.

Examinations are held at the above Institute.

NEXT TERM commences SEPTEMBER 16th, 1904.

Courses are so arranged that Students can do the work on Saturday and one evening per week.

Full particulars can be obtained on application to the DIRECTOR OF EDUCATION.

CITY OF LONDON COLLEGE, WHITE STREET and ROPEMAKER STREET, MOORFIELDS, E.C.

MICHAELMAS TERM commences OCTOBER 3rd.

CLASSES and LABORATORY WORK in CHEMISTRY, PHYSICS, BIOLOGY, BOTANY, GEOLOGY, and PHYSIOLOGY. Special preparation for the Examinations of the Pharmaceutical Society, The Conjoint Board. Complete Courses for University Matriculation and Inter. and Final B.Sc., meeting during the Evening and on Saturday.

Full particulars gratis on application to—

DAVID SAVAGE, Secretary.

SILICATES OF SODA and POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.

FULL STRENGTH GUARANTEED.

OLDEST and MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.

LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.



RADIUM BROM.

POLONIUM.

RADIO-ACTIVE ORES.

BAR.-PLAT. CYAN. SCREENS.

" LARGE CRYSTALS.
ETC., ETC.,

ALL AT REASONABLE PRICES.

Armbrrecht, Nelson & Co.,

71-73, Duke-st., Grosvenor-sq., W.

'Phone—4942 Gerard.

CARPENTERS' COMPANY'S

TECHNICAL INSTITUTE, JUPP ROAD, STRATFORD, E.

CLASSES

IN

SCIENCE, ART, TECHNOLOGY, and LANGUAGES.

Chemical and Physical Laboratories.

Manual Training.

Workshops for PLUMBING, ENGINEERING, CARPENTRY
and JOINERY, &c., WOOD-CARVING.

OPENS on MONDAY, SEPTEMBER 19th.

Prospectus on application.

EAST LONDON TECHNICAL COLLEGE, MILE END ROAD, E.

Session 1904-1905, commencing September 19, 1904.

DAY and EVENING COURSES for the

B.Sc. (Honours and Pass) Degree of the University of London are conducted by the following Lecturers, who are recognised teachers of the University of London:—

Mathematics	{ J. L. S. HATTON, M.A., and
Physics	{ W. F. S. CHURCHILL, M.A.
Chemistry	{ R. A. LERFELDT, D.Sc., &c.
Botany	{ J. T. HEWITT, D.Sc., Ph.D., and
Engineering	{ C. SMITH, D.Sc.
Electrical Engineering	{ V. H. BLACKMAN, M.A.
	{ D. A. LOW, M.I.M.E.
	{ J. T. MORRIS.

The Day Courses in ENGINEERING and CHEMISTRY are also suitable for those entering manufacturing firms.

Calendar 24d. post free on application.

J. L. S. HATTON, Director of Studies.

THE CHEMICAL NEWS

Vol. XC., No. 2340.

THORIUM; CAROLINIUM, BERZELIUM.*

By CHARLES BASKERVILLE, Ph.D., F.C.S.

(Concluded from p. 153).

METZGER has published an interesting and novel method for separating thorium from cerium, lanthanum, and the didymium depending upon its precipitation from a neutral solution by a 40 per cent alcoholic solution of fumaric acid (*Journ. Am. Chem. Soc.*, xxiv., 901). The writer and Lemly† have verified these observations, as far as ordinary analytical methods are concerned. Applying it to the accepted chemically pure thorium, however, we obtained a filtrate less than one-half of 1 per cent, which, on evaporation and ignition, gave a greyish oxide possessing such marked radio-activity by the electrical method, that Dr. Pegram stated it acted as if "salted with radium."‡ This decayed very rapidly from 42 to 12.4 in eight days, to 3.3 in nine days more (uranium being taken as standard at unity). After thirty-two days more it gave 3, and was practically constant. The corresponding values obtained for the thorium precipitate, which constituted virtually the whole, were 0.63, 0.92, and 1. Truly but one interpretation of these results may logically be had, namely, the existence of a radio-active body with thorium, which is different from it. Crookes has sounded a timely warning against depending upon the photographic method for determining the radio-activity; so we have been guided mainly by the electrical method. Yet most interesting observations may be had by the photographic method, which has been used to secure very rough quantitative results, but by no means comparable to the other procedure. It aids one much in learning the β -activity, whereas the α -rays are the most important factor in the ionisation of gases upon which depends the electrical method. Persistent differences in radio-activity of the preparations had by different chemical methods have been noted, and the same method of preparation has given persistent differences in radio-activity measured by the same and different methods.

Rutherford (*loc. cit.*) and the Curies (*loc. cit.*) have shown that the α -radiations, or "emanations" according to the former, as adverted to, are readily driven away from radium halides and thorium oxides and condensed by liquid air. It does not come within the scope of this paper to discuss the nature of these emanations, which will be dealt with by the author and Lockhart§ in another communication. Suffice it to say that we have repeated this work successfully, and we have applied the same test to a large number of authenticated radio-active minerals, and in every case where those minerals have been known to contain helium we have succeeded in condensing the emanations from them. We have obtained the emanations from uranium and thorium bearing minerals, and we have failed to secure emanations condensed on a fluorescent zinc sulphide screen from minerals containing thorium.

The extremely interesting work by Rutherford, with his able associate, Soddy, and their students, on the regeneration of Thorium X, at first thought would apparently convince one that thorium is primarily radio-active, but this can be explained by the presence of minute amounts of a foreign highly active substance, which, so far, has failed

to be sufficiently concentrated for a thorough chemical examination, and yet exercises continually the novel property of inducing radio-activity. It is not hazardous to venture the opinion that it will prove to be actinium. In the light of the facts enumerated, however, it appears that thorium is not primarily a radio-active body any more than water containing a radium salt is primarily radio-active, because the radio-activity appears therein after it is distilled. It must be distinctly understood that no criticism is being passed upon the brilliant investigations progressing so successfully in the McGill laboratory on this extraordinary phenomenon of radio-activity, whatever be its source. It must be remembered that radio-activity is far more delicate than the spectroscopy; consequently a notable per cent of a body possessing that property may be present before any spectroscopic evidence may be had, as noted in Demarcay's work on radium. Further, the compounds of this element exhibit unusual radio-active strength before any change whatever is measurable in the atomic weight of the barium with which it is associated.

Although we have not as yet secured a thorium preparation free from any radio-activity, our observations confirm those of Rutherford and his co-labourers. The conclusion thus arrived at is that thorium as ordinarily extracted from mixed or complex minerals contains a primary radio-active body, perhaps similar to the truer thorium, but not necessarily so.

From what has been said, that which follows may be considered as if there were no such thing as radio-activity, as the amount of the body possessing that property is entirely negligible, from a spectroscopic standpoint, and far too small to produce the marked physical and chemical changes in pure thorium now to be briefly recounted.

Some years ago the writer and Davis began work on the atomic weight of thorium. A full account of the objections to the former methods will be given in due time. Working with materials from various sources such variable results were obtained that they could not be attributed to faulty methods. In the light of the research of Brauner and the observations made in this laboratory, the problem resolved itself into securing a pure substance, as free from its contaminating constituents as possible.

In the work of Jefferson and Smith on the separation of the rare earths by means of organic bases, it was stated that thorium gives a yellow precipitate with phenylhydrazine ("Aromatic Bases as Precipitants for Rare Earth Metals," *Journ. Am. Chem. Soc.*, 1902, xxiv., 540). Allen remarks that with pure thorium and pure phenylhydrazine the precipitate is white and quantitative (*Journ. Am. Chem. Soc.*, xxv., 421). Although Allen does not state that the source of this material was free from uranium, it may be that both of these observations are correct, as noted previously by the author and Lemly.* The precipitate produced by phenylhydrazine with very pure thorium is at first white and gelatinous, but soon acquires colour, doubtless due to decomposition of the precipitant. We have observed that fractionation of thorium can be brought about by means of phenylhydrazine. By addition of an insufficient amount of the reagent one obtains first a heavy flocculent precipitate, which soon acquires colour. On addition of more of the reagent there is obtained a gelatinous, white precipitate, which also acquires colour as the precipitant decomposes. These substances are different, as shown by variations in the radio-activity determined by both methods, and the solubility of the oxides in hydrochloric acid.

So far we have found it impracticable to fraction thorium compounds on a large laboratory scale with phenylhydrazine. The gelatinous precipitate clogs up the filtering media we have tried. Upward suction through unglazed porcelain, which has served so satisfactorily in much of the work on the rare earths in this laboratory, failed utterly.

* Presented before the New York Section of the American Chemical Society, April 8, 1904.

† Unpublished work.

‡ Personal correspondence. In time Dr. Pegram will no doubt publish a full discussion of all the results.

§ Soon to be published.

* Unpublished work. Reported in abstract at the Pittsburg meeting, 1902.

Attention must be directed to the fact that all the different constituents are precipitated by this reagent, but at different rates; hence the speed of the reactions was the point of attack. The difficulty was not one of simple filtration, which may be carried out readily enough after the precipitates have formed and settled, but of rapid separation, thus avoiding a second formidable hindrance, namely, decomposition of the phenylhydrazine with corresponding variations in the reactions. The use of a centrifuge offered promise. It was successful, and perhaps may be used on a commercial scale, although for reasons which follow it is not recommended. With the machine at our disposal we could work with but 20 c.c. at a time. The solution must be weak, and a small batch amounted to 10 litres. We regarded it essential that sufficient material be prepared for further purification and investigation, an ample supply being at hand through the generosity of the Welsbach Lighting Company. The writer did not feel that he had more time than the average allotment of life to a chemist, thirty years, so attempted a rough and ready settling and decantation with one lot of 10 litres, but with poor success. The old fractional precipitation of the rare earths by ammonia, complained of by Crookes, Hood, and others, is mere child's play in comparison with the time robbing and indefinite fractionation by this aromatic base. A separation of thorium into different constituents was brought about, as shown by atomic weight determinations of different portions. Fractions were had (as tetrad) giving 214, 228, 235, 242, 249, and 252; the original giving 232.5 and 232.6.

This procedure was temporarily abandoned to make use of the method earlier pursued in fractionation, and later in the efforts of Dr. Davis and myself to determine the atomic weight of thorium, namely, preparation of the pure crystalline tetrachloride by heating pure thorium dioxide mixed with pure sugar carbon in an atmosphere of chlorine. It is unnecessary in this paper to give the details of our procedure, which will be described later in full, further than to say we found it inadvisable to use hard combustion glass tubing, as variable amounts of contaminating chlorides were formed from the glass. We found we could not settle upon a definite correction for these impurities, as did Richards in his elegant work on uranium ("Atomic Weight of Uranium," Richards and Merigold, CHEMICAL NEWS, 1902, lxxxv., 177, 186, 201, 207, 222, 229, 249).

Quartz tubes, 2 c.m. in diameter made to order, were placed within large porcelain tubes, which rested in a powerful combustion furnace. A carbon boat containing the mixture of thorium oxide and carbon was inserted in the end of the quartz tube. Pure chlorine free from oxygen was carefully dried, as it issued from a cylinder, by elaborate desiccating apparatus, and led in by means of a smaller quartz tube, so that the stream of gas played directly into the boat. Arrangements were made by glass cocks to prevent a back flow of any volatile body that might be produced.

As previously noted by Berzelius and the author, when this method is followed out, there is obtained a volatile chloride, "weisser dampf," absorbable by alcohol, which, according to the former, is *not* thorium, yet comes from pure compounds of that element. This has been verified by applying the method to thorium obtained from a number of sources, including a small amount of very pure preparation used by Cleve in his atomic weight determinations, and presented to Dr. F. W. Clarke, of Washington, who kindly loaned the preparation to us. It therefore appears that the volatile chloride is to be had from thorium itself, or that material which separates with thorium in its extraction from various minerals.

Beautiful fern-like crystals of thorium tetrachloride formed on the inner walls of the quartz tubes. There remained in the carbon boat variable amounts of residue, largely converted into chloride, depending upon the temperature of the furnace and duration of the heating from two to ten hours. These accumulated residues were converted into the oxide and subjected to similar treatment

several times. With each repetition there were diminishing amounts of the volatile chloride and sublimed thorium tetrachloride formed. After the third re-distillation the oxide from the residue was digested in hydrofluoric acid and concentrated hydrochloric acid to remove accumulated impurities from the carbon and quartz tube. This oxide is *soluble in concentrated hydrochloric acid*, from which it may be crystallised by evaporation. This is not the novel thorium oxide, Th_2O_3 , described by Locke (*Zeit. Anorg. Chem.*, 1894, vii., 345), or that unique compound of thorium which has caused the spirited controversy between Stevens (*Ibid.*, 1901, xxvii., 41; 1902, xxxi., 368) and Wyruboff and Verneuil (*Ibid.*, 1901, xxviii., 90; 1902, xxxii., 376). The material thus obtained gave an atomic weight of 241.7 (tetrad).

This chloride was re-crystallised from concentrated hydrochloric acid three times, until the fine white needle-crystals appeared the same. The material was converted into the oxide by solution in water, in which it was readily soluble, giving a perfectly clear solution absolutely devoid of any opalescence (see Locke's chloride), precipitated by ammonia, and the washed white gelatinous hydroxide ignited in platinum. It was digested in turn with dilute hydrochloric, nitric, and hydrofluoric acids, washed with pure water, and brought to a constant weight.

In our first published work on thorium some store was laid by the specific gravities of the oxides of the several fractions as a means for watching the course of the disintegration. Some doubt was thrown upon this method of control through work of the writer and Mills,* as variations in the value of the same preparations were had depending upon the method employed. It was learned, however, that satisfactory comparable figures were obtained when the oxide was prepared in the same way each time.

The specific gravity of this oxide was determined:—

Amount taken. Grm.	Specific gravity.
0.7992	11.25
0.8973	11.27

The specific gravity of the original pure thorium oxide:—†

Amount taken. Grms.	Specific gravity.
2.0730	10.54
3.4573	10.51

The atomic weight was then determined:—‡

Oxide used.	Sulphate obtained.	Equivalent.	Atomic weight.
1.559290	2.434914	63.875	255.5
0.524254	0.819365	63.975	255.9
0.549331	0.854810	63.900	255.6

The familiar method used was essentially that of G. Krüss with certain variations, namely, a specially devised platinum lined asbestos jacketed bath was used, and the temperature judged by a thermometer in which mercury was under a pressure of 20 atmospheres, capable of registering 560° C. It was standardised by the Reichs-Anstalt.

It is scarcely the time or place to discuss the sulphate method, which will be dealt with fully later. It is well known that the method does not possess the most desirable degree of accuracy, but it answers entirely for such work as is here reported (see "Rare Earth Crusade," *Science*, N.S., May 15, 1903; CHEMICAL NEWS, lxxxviii., 18). The treatment with new amounts of sulphuric acid was continued until constant weights were had. It is, perhaps, just as well to state that the weights used were gold plated and corrected by the Bureau of Standards in Washington. The vibration method was used with a highly sensitive

* Unpublished.

† This work was done by the writer and S. Jordan, and will later be published in full.

‡ Unpublished—by the author and R. O. E. Davis.

Sartorius balance* resting upon a brick-cement pillar, and that the pans were so loaded each time with counterpoises and standardised platinum weights as to bring the apparatus to a determined point of the highest sensitiveness. Further, it may not be out of place to state at this point that after removal from the porcelain tube the material used did not come in contact with anything other than Jena glass and platinum; that the water, acids, and ammonia used were re-distilled in platinum, and gave no weighable residues after evaporation. The sulphuric acid was not re-distilled, but the very fine product especially secured gave no residue on evaporation of 50 c.c., and if it had it would have tended to lower the atomic mass value.

It is here quite interesting to note that Hofmann and Zerban (*Ber. Chem. Ges.*, 1903, xxxvi., 3093) state that the equivalent of "actinium" has been found to be 63.32, or 253.28 atomic weight, whereas that for pure thorium is 58.1, or 232.4 (O=16). Carolinium oxide shows a radio-activity of 0.56 and 0.6 (original thorium oxide = 1) by the electrical method. The two values were obtained from the same material after an interval of six weeks. Our preparation on heating almost to white heat gave off no "emanation" condensable by liquid air upon a zinc sulphide screen.

The volatile chloride was collected in part by its absorption in alcohol and condensation as acicular crystals in the cooler portions of the porcelain tubes. These were dissolved in water and the whole evaporated to dryness, the oxide digested by turn in hydrofluoric, concentrated hydrochloric, and nitric acids, and then dissolved in hot sulphuric acid (1:1), the gelatinous white hydroxide precipitated by ammonia, washed, and ignited to a constant weight in platinum.†

The specific gravity of this oxide was determined:—

Amount taken.	Specific gravity.
1.9207	8.442
1.8465	8.512

(On p. 766 in my former paper (*loc. cit.*) small amounts of oxides were obtained giving specific gravities 8.77, 8.47, and 11.26).

The atomic weight obtained, assuming its tetravalence:—

Oxide used.	Sulphate found.	Equivalent.	Atomic weight.
0.306778	0.505705	53.375	213.5
0.320618	0.530890	53.000	212.0
0.794692	1.309245	53.175	212.7

It is very interesting to note that the oxide obtained from this volatile chloride possesses very slight radio-activity, about one-third that of the original thorium when tested by the electrical method. An exposure to a sensitive photographic plate for seventy-two hours showed that it possesses radio-activity which affects the photographic plate to a very limited degree. It does not give off emanations condensed at the temperature of liquid air as judged by the effect on a phosphorescent zinc sulphide screen.

Although we know that this material is not yet pure, for reasons which will be given in the following, the novel properties mentioned above and its contrasting chemical conduct enumerated below, warrant the statement that we have a new element. Berzelius was the first to observe the formation of this "weisser dampf." On account of his beautiful pioneer researches in the difficult field, as the discoverer of thorium from which it comes, it is only proper that it should bear his name, so I have designated the element *Berzelium*, with the symbol Bz.

Just a few words concerning the new thorium, or thorium freed in a measure from carolinium and berzelium, are called for here, as that element will be treated of more fully in a later communication. In our former paper (*loc. cit.*,

p. 771) the values obtained for the atomic weight of thorium from the tetrachloride were 222–223.3. It was distinctly stated that the values were preliminary, and are not to be taken as final on account of the small amount of material used in each determination. More material has been secured, purified by treatment with acids, as mentioned above, and atomic weight determinations made according to the sulphate method. Following are the values found:—

Oxide used.	Sulphate found.	Equivalent.	Atomic weight.
0.425456	0.694934	55.15	220.6
0.740052	1.210405	55.025	220.1

Doubtless Chroustschoff's russium and Brauner's thorium a were quite pure preparations of thorium.

The source of heat for our furnace was gasoline gas, which does not have a constant pressure; consequently there can be no question but there is present in this middle portion variable but small amounts of carolinium and berzelium, and that some thorium is in the two extremes. We have just received a specially constructed electric oven from Heraeus and a Le Chatelier pyrometer, so that the process may be controlled with precision. This apparatus has been purchased through a grant from the Carnegie Institution received this year.

Although these constituents are not yet in the most desirable and highest state of purity, it became important to learn their comparative conduct under certain influences, physical and chemical.

It may be recalled that Kunz (*Science*, N. S., 1903, xviii., 769) and the author examined the action of ultra-violet light, Röntgen rays, cathode rays, and the complex radiations and emanations of radium rays upon a large number of gems and minerals in the Morgan-Tiffany and Morgan-Bement collections of the American Museum of Natural History in New York. At that time the writer also observed the action of many of the rare earth oxides of ultra-violet light produced by sparking high voltage currents between iron terminals (*CHEMICAL NEWS*, lxxviii., 262; *Am. Journ. Sci.*, 1903, xvi., 465). The dioxides of zirconium and thorium only became phosphorescent under such stimulation. One is radio-active, the other not. Uranium oxide, which is radio-active, did not respond. The new thorium oxide phosphoresced beautifully white on a five minute exposure, while berzelium and carolinium oxides gave negative results. Carolinium oxide containing variable amounts of thorium responded in proportion to the latter constituent present. We believe this is perhaps the first application of the method to the examination of material in the course of chemical investigations, as suggested by Kunz and Baskerville.

We have learned that ordinarily accepted pure crystalline thorium chloride, when thrown upon a filter-paper from concentrated hydrochloric acid, may be washed with water, a clear solution resulting. Berzelium and carolinium chlorides act similarly. When thorium is freed from these, the body will remain upon the filter-paper, and may be washed with concentrated hydrochloric acid, but as soon as pure water is added it hydrolyses and gives a turbid filtrate, acting in exactly the same way that titanium does. This was not suspected, although after the observation was made (by Jordan in this laboratory) it is no more than one might expect. As zirconium does not act like titanium, the natural inference is that it contains some hindering element, perhaps the earth reported by Hofmann and Frandl in zirconium from euxenite (*Ber.*, 1901, xxxiv., 1064).

The hydroxides of these three substances are white and gelatinous, insoluble in ammonium, sodium, or potassium hydroxide, readily soluble in the ordinary acids. Carolinium oxide is greyish with pink tinge, thorium white with merest tendency towards green, and berzelium has a more marked leaning towards green. These remarks are applicable to the substances in that state of purity so far had. The oxides of thorium and berzelium are not soluble in hot concentrated hydrochloric acid even when the digestion has lasted three weeks. Carolinium oxides dissolves slowly but completely within a few days, and the chloride forms

* Constructed for Dr. F. P. Venable; see his work on Zirconium, *Townsend Chem. Soc.*

† I have been assisted in this part of the work by P. Irwin.

fine crystals on concentration of the solution, quite different from ordinary thorium chloride. All three are readily precipitated by the ordinary thorium reagents, viz., ammonium oxalate, sodium thiosulphate, hydrogen dioxide, potassium periodate, &c. Their salts behave differently with various organic bases. Phenylhydrazine after a time in the cold gives a precipitate which becomes yellow, berzelium red, and thorium orange. Pyridine precipitates thorium at once, carolinium slowly, and berzelium with extreme slowness and incompletely. Xylidine precipitates both the former, but not berzelium. *o*-Toluidine gives a pinkish precipitate with thorium, a white flocculent one with carolinium, and none with berzelium. Thorium is completely precipitated by fumaric acid, carolinium only partially, a clear filtrate being had in both cases. Berzelium is precipitated nearly completely by fumaric acid; the filtrate is rendered opalescent by ammonia, however.

The solutions of none of these gave absorption bands. Dr. W. J. Humphreys, of the Rouss Physical Laboratory, University of Virginia, kindly examined the arc spectra with a Rowland grating, twenty-one feet in diameter, and 20,000 lines to the inch. His examination, covering the region between 3900 and 5500, showed some differences between berzelium and the other two, but his conclusion was that the differences in the spectra of those portions of the three materials which give arc spectra might be accounted for by impurities, or at any rate were not sufficient to warrant the statement from his spectral data that they are not the same.

Small portions of the impure materials have been sent to Sir William Crookes, by request, to be examined in the ultra-violet region with the apparatus used in his beautiful mapping of the spectrum of radium.

Summary.

1. The preponderance of evidence indicates that thorium is not a primary radio-active body.
2. There can be no question from the work of Chroustschoff, Brauner, Crookes, Rutherford, Auer, and the author, but thorium is complex and not a chemical element as we accept the term.
3. From the experimental data, physical and chemical, outlined in this communication, it appears that thorium has been resolved into at least three simpler substances, and that they are sufficiently identified to deserve distinct names.
4. The conservative position, in which the author coincides, concerning the acceptance of novel members of the family of elements, is the requirement of spark spectral confirmation. At the same time it must be kept in mind that even spectral work requires unification.*
5. As stated above, one of the objects of this paper is to present work to guide others, and seek confirmation in other hands. While we shall be busied with the investigation, instead of asking a reservation, we would invite others to assist in solving the problem.

University of North Carolina
April, 1904.

Addendum.

Since the paper was written and presented, a letter from Sir William Crookes has been received, excerpts from which are given herewith. "I had not quite sufficient to enable me to photograph the whole ultra-violet spectrum, but I have taken that portion, between wavelengths 3444.020 and 4071.903, which contain some very characteristic thorium lines. I compared the spectra with my standard thorium spectrum taken from the spark between poles of metallic thorium. Making allowance for the fact that my spectrum is from the metal, while that from your material is from the chloride solutions, the five spectra are practically identical, all the prominent lines being seen in each spectrum, while there are no lines in one

which are not seen in the others. . . . You must not attach too much importance to these spectrum results. All I can say is that they give no positive proof of the existence of anything new. But they by no means prove that such bodies do not exist. They may be there with their spectra masked by the thorium which is present."

As only a limited portion of the spectrum was examined, the question is still an open one. My sincere thanks are due to Sir William Crookes.

June 18, 1904.

ISOMERISM OF α - AND β -CROTONIC ACIDS.*

By R. S. MORRELL AND E. K. HANSON.

THE isomerism of α - and β -crotonic acids has been investigated by a number of chemists, amongst whom the names of Geuther, Michael, and the late J. Wislicenus are most prominent. Michael (*Journ. f. Prakt. Chem.* [2], xlv., 236) has described the method he used to obtain the β -crotonic; and Wislicenus, by a modification of the same method, obtained the β -acid in the crystalline condition.

In an earlier communication (Morrell and Bellars, *Journ. Chem. Soc.*, lxxxv., 345) use was made of the quinine salt for the separation of the β -acid from its isomer contained in the ordinary "isocrotonic acid." It is quite easy to separate the quinine β -crotonate from the α -crotonate by fractional crystallisation, as the former is much less soluble in water. From the quinine salt, barium β -crotonate was next prepared, and, by acidifying with dilute sulphuric acid and extraction with ether, crotonic acid melting at 15° C. was obtained in the form of feathery needles, which possessed all the properties ascribed to it by Michael and Wislicenus.

The present investigation divides itself into two parts:—
1. Observation of the depression of the freezing-point of the isomeride by addition of the other.

2. Determination of the equilibrium mixtures in the liquid condition at varying temperatures.

The freezing-point curve is a continuous one, and there is a eutectic point at a temperature not far from -3° C.

It will be noticed that no mixture gave a freezing-point approaching -20°, whereas the so-called "isocrotonic acid" does not solidify at -20° C.

This point is one of great interest, and it seems to us possible that the explanation may lie in the formation of a compound between the α - and β -acids at temperatures above the melting-point of the α -acid. This compound could easily form a eutectic mixture with the β -, or even with the α -acid. This might not solidify at -20°. Light, it is hoped, will be thrown upon this by the second part of the work, which is as yet incomplete.

THE CONSTITUTION OF PHTHALEIN SALTS.†

By Prof. RICHARD MEYER.

THE author presented a report on his experimental work on the constitution of phthalein salts at the last *Versammlung Deutscher Naturforscher und Aerzte*, at Cassel (*Ber.*, 1903, xxxvi., 2949).

Phenolphthalein itself is colourless, and is generally regarded as a lactone, whilst the quinonoid formula is assigned to its red alkali salts by the majority of chemists. Fluorescein, being coloured both in the free state and in the form of salts, is regarded as being quinonoid either when free or combined.

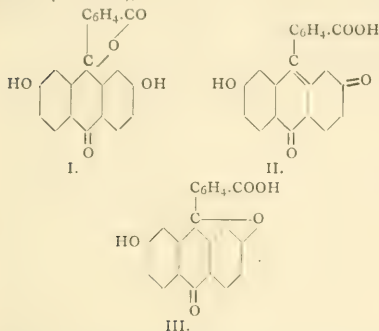
Quinolphthalein (I.), the constitution of which has been confirmed by work done in the author's laboratory, does

* Abstract of a Paper read before the British Association (Section B), Cambridge Meeting, 1904.

† Read before the British Association (Section B), Cambridge Meeting, 1904.

* See my Address before Section C, American Association for the Advancement of Science, St. Louis Meeting, December, 1903.

not come into quite the same category, and its red alkali salts must be supposed to possess a meta-quinonoid constitution (II. or III.),—



Metaquinones being at present unknown, further work on the above substances was desirable, and the author and his assistant, Mr. O. Sprengler, have therefore studied the ethers and oximes of phenol- and quinol-phthalein, preparing these substances in alkaline solution; the results of this work point to the lactonic formula of the alkali salts as being correct, both in the case of quinolphthalein and of phenolphthalein. They drew attention recently to the fact that the anilides of the phthaleins dissolve in alkali without giving rise to colouration; if these anilides have the same constitution as the phthaleins themselves, this distinction might arise from a difference in basicity. They therefore endeavoured to ascertain the equivalents of these substances. A measured volume of standard caustic soda solution was treated for two hours at the ordinary temperature with an excess of phenolphthalein; in a second and a third experiment quinolphthalein and phenolphthalein anilide was subjected to similar treatment. The undissolved residue was filtered off and washed, the filtrate being then precipitated with dilute sulphuric acid; the precipitates were filtered, washed, dried, and weighed. The results agreed with the formulæ $C_{20}H_{12}O_4Na_2$, $C_{20}H_{10}O_5Na_2$, and $C_{20}H_{12}O_3(NC_6H_5)Na_2$. Thus all three compounds behave alike as dibasic acids, and from this point of view no difference is traceable between the anilide and the free phthaleins; the anilide is, however, more feebly acidic than the phthaleins, being precipitated by the latter from its alkaline solution.

These experiments have some bearing on those published recently by A. G. Green and A. G. Perkin, but the results of these investigators differ from the present because they worked under different conditions.

The authors have made many attempts under varied conditions to obtain a quinonoid ether of phenol- or quinolphthalein, employing methyl-iodide and methyl sulphate, both in aqueous and alcoholic solutions, and using an excess of alkali and also of sodium methoxide. In each case the same di-ethers as before were obtained; they are colourless, and doubtless possess a lactonic constitution. Only when the neutral sodium salts of the two phthaleins are treated, two new compounds are formed in addition to the well known di-ethers. These substances proved to be the mono-ethers, $C_{20}H_{12}O_3.OCH_3$ and $C_{20}H_{11}O_4.OCH_3$, and are not carboxylic but hydroxylic ethers; they could not be saponified, and on further treatment with alkyl salts yielded the lactonic ethers. They do not decompose sodium carbonate, and hence do not contain a free carboxyl group; moreover, they are colourless, and are doubtless of lactonic constitution, just as are the di-ethers. They form, however, red salts, the constitution of which is open to discussion.

The quinonoid formulæ of the phthaleins indicate the presence of one carboxyl and one phenolic hydroxyl group in the molecule, whilst, according to the lactonic formula, two phenolic hydroxyl groups are present. The etherification conditions of carboxylic acids and phenols were therefore studied, as it appeared of prime importance to ascertain whether the carboxyl group can be esterified under the conditions prevailing in the present experiments, namely, in neutral or alkaline solution. The following facts were established as the result of numerous experiments carried out under a great variety of conditions:—Phenol is always converted into its ethers by means of alkyl halogen salts and by methyl sulphate, whether the solution be alkaline or neutral, or even acid; the only point of difference is in the yield obtained. Benzoic acid, however, can only be esterified in acid or neutral solutions, but not in alkaline ones, whether alkyl halogen salts or methyl sulphate is used.

It would seem difficult to reconcile the above results with the quinonoid formula of the phthalein salts; the difficulty involved in the assumption of the quinonoid theory is also felt by A. G. Green and A. G. Perkin, and they attempt to overcome it by assuming the intermediate formation of the carbinol salt. This view would indicate that the red solution contains, in addition to the quinonoid salt, a certain proportion of carbinol salt, from which latter the lactonic ethers are produced; and that during the course of the reaction the quinonoid salt is progressively converted into carbinol salt, in accordance with the law of mass action, until the change has become complete. The carbinol salt could only be formed by opening the ring, and this could only take place whilst working in presence of excess of alkali; since, however, the author has obtained the same lactonic di-ethers in neutral solution, the opening of the lactonic ring in this case would appear to be impossible.

The advocates of the quinonoid theory point to analogies between phenolphthalein and fluorescein, but the author is of opinion that it would be very difficult to find, in one group of chemically related compounds, two substances more dissimilar than are phenolphthalein and fluorescein. Thus, for instance, R. Nietzki and P. Schroeter obtained one lactonic and three quinonoid ethers by the alkylation of fluorescein, whilst the salts of phenol- and quinolphthalein never yielded quinonoid derivatives under the most varied conditions of working. The quinonoid ethers of tetrabromophenolphthalein, discovered by R. Nietzki and E. Burckhardt, have no bearing on this question, because they have not been prepared from the phthalein salts. It would be preferable to try to express the different behaviour of fluorescein and phenolphthalein by the aid of chemical formulæ rather than to insist on a similarity which is not warranted by the facts.

One serious difficulty arises in connection with the colour of the alkali salts. Ostwald assumes that the red colour is due to the phthalein ions, whilst the undissociated molecules are colourless. If, however, the ions are coloured, they should contain a chromophoric group, such as is present in undissociated coloured molecules; the lactonic formula does not indicate the presence in the molecule of such a chromophoric group. At the same time, it must be agreed that, however valuable the theory of chromophors has proved as a means of characterisation and classification of colouring matters, it is not sufficiently comprehensive to include all coloured organic compounds. It does not include the quinolphthaleins (and orcinphthalein), dibenzalacetone, and other colourless substances which form feebly coloured addition compounds with mineral acids. Adolf Baeyer introduced the term "halochromy" as descriptive of this phenomenon, and it does not seem impossible that the colour of phthalein salts is due to a kind of halochromy.

The author is continuing his work in another direction, and hopes to obtain further evidence bearing on this question.

NOTE ON

THE INFLUENCE OF RADIUM RADIATIONS
ON ATMOSPHERIC OXIDATION
IN PRESENCE OF IRON.*

By HENRY J. HORSTMAN FENTON, F.R.S.

It has been pointed out by the author in previous communications (*B. A. Report*, 1895 and 1898) that the oxidation of certain hydroxy-compounds, such as tartaric acid or glycol, in presence of iron, may be brought about by atmospheric oxygen in presence of sunlight, and that the products are the same as those obtained when hydrogen dioxide is employed as oxidising agent. It is now found that the influence of radiations from radium bromide may, in certain cases, produce effects similar in this respect to those obtained by exposure to sunlight. A solution of tartaric acid, for example, containing a small quantity of ferrous tartrate, was divided into two parts and kept in the dark in presence of air, one of the tubes being placed directly over a specimen of radium bromide. On testing the solutions after a day or two with phenylhydrazine acetate a very striking difference was observed in the results, the exposed solution giving the larger yield of Nastvogel's osazone.

THE

STUDY OF HYDRO-AROMATIC SUBSTANCES.†

RECENT WORK ON HYDRO-AROMATIC SUBSTANCES.

By Dr. A. W. CROSSLEY.

THE following is a summary of the work published on hydro-aromatic compounds since the preparation of the last report (*Reports*, 1903, p. 179).

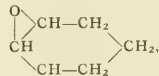
Petroleum.—Roumanian petroleum (Poni, *Journ. Chem. Soc.*, 1903, Abstract, [1], 593) resembles Russian and American petroleum, inasmuch as the densities of fractions taken every 2° between 50° and 70° diminish to a minimum at 60° to 62°, and then continuously increase, whilst in the case of Galician oil there is a steady increase of density throughout. A further difference from this latter oil is to be found in the composition of the fractions between 60° to 100°, which do not contain secondary hexanes, as on nitration they yield aromatic derivatives only. Methyl- and ethyl-hexahydrobenzene are among the hydrocarbons contained in the Roumanian oil.

Hydrocarbons.—Sabatier and Senderens (*Comptes Rendus*, 1901, cccxii., 1254) have shown that, when benzene or its homologues, containing methyl groups as side-chains, are passed together with hydrogen over reduced nickel, hydrogenation takes place without complication; whereas if the hydrocarbons contain longer side-chains (ethyl, propyl, &c.) part of the latter is split off. For example, ethylbenzene gives principally ethylhexahydrobenzene, but also small amounts of methylhexahydrobenzene. Sabatier and Mailhe (*Comptes Rendus*, 1903, cccxvii., 240) have further investigated the product obtained by passing benzene and hydrogen over reduced nickel, and find that if the temperature be maintained at 250° pure hexahydrobenzene is formed, identical in all respects with that occurring in Caucasian petroleum. If hexahydrobenzene be passed over reduced nickel at 270° to 280°, it is decomposed into benzene and hydrogen, which latter reacts with the benzene, forming methane. An energetic substitution reaction takes place when chlorine acts on hexahydrobenzene at a temperature of 0°, resulting in the formation of a mixture of mono-, di-, tri-, tetra-, and hexachloro-derivatives (*Bull. Soc.*, 1903, xxix., 974).

According to Markownikoff (*Cent. Blatt.*, 1904, [1], 1345), methylhexahydrobenzene has not been obtained pure by the methods so far described; for example, when isolated from Caucasian petroleum, it is contaminated with normal heptane. It can, however, be prepared in the pure condition by the action of zinc dust on an aqueous alcoholic solution of 3-bromo-1-methylhexahydrobenzene. The hydrocarbon obtained by eliminating the elements of hydrogen bromide from this latter substance is a mixture of the two methyltetrahydrobenzenes with the double bonds in the 2:3 and 3:4 positions (*Cent. Blatt.*, 1904 [1], 1346). The pure substances have been obtained by other methods (*Cent. Blatt.*, 1903, [2], 289; 1904, [1], 1213; Wallach, *Annalen*, 1903, cccxxix., 368). In such hydrocarbons the influence of the side-chain is such that in the splitting off of hydrogen together with a halogen, or in the combination with a molecule containing mobile hydrogen, the latter splits off from, or combines preferably with, the carbon atom furthest removed from the side-chain, whilst the electro-negative element combines with the carbon nearest the side-chain, i.e. 1:3-trimethyl- Δ^4 -tetrahydrobenzene (Harries and Weil, *Ber.*, 1904, xxxvii., 848).

Hydroxy-derivatives.—The reaction introduced by Sabatier and Senderens has been extended to the preparation of aromatic alcohols. When phenol is passed together with excess of hydrogen over reduced nickel at a temperature of 140–160°, pure hydroxyhexahydrobenzene is obtained (Holleman, *Cent. Blatt.*, 1904, [1], 727; Brunel, *Comptes Rendus*, 1903, cccxxvii., 1268; Sabatier and Senderens, *Ibid.*, 1903, cccxxvii., 1025); but if the temperature be raised to 215–230°, the hydroxyhexahydrobenzene first formed is decomposed into ketohexahydrobenzene and hydrogen. From the mixture so produced Sabatier and Senderens have obtained the pure alcohol or ketone by, in the first case, passing the product with excess of hydrogen over reduced nickel at a temperature of 140–150°, and in the second by passing the product without hydrogen over reduced copper at a temperature of 330°. Under similar conditions thymol and carvacrol are converted into the corresponding hexahydro-derivatives (Brunel).

Iodo-hydroxyhexahydrobenzene gives, when treated with potash or silver oxide (Brunel, *Comptes Rendus*, 1903, cccxxvii., 62), the internal oxide of 1:2-dihydroxyhexahydrobenzene,—



into which substance the former is easily converted by the action of water. When the internal oxide is treated with alcoholic ammonia (Brunel, *Comptes Rendus*, 1903, cccxxvii., 198), there result 1-amino-2-hydroxyhexahydrobenzene and two forms of dihydrocyclohexylamine, $\text{NH}(\text{C}_6\text{H}_{10}\cdot\text{OH})_2$.

Power and Tutin have isolated a laevorotatory modification of quercitol from the leaves of *Gymnema sylvestre* (*Journ. Chem. Soc.*, 1904, lxxxv., 624). It is demonstrated that this substance has the same constitution as d-quercitol (pentahydroxyhexahydrobenzene) which has been established by Kiliani and Schaefer (*Ber.*, 1896, xxix., 1762), and can only differ from the latter stereochemically; but, since d-quercitol has $[\alpha]_D + 24.16^\circ$, whilst the new quercitol has $[\alpha]_D - 73.9^\circ$, the one cannot be the optical antipode of the other. Eight optically active modifications of pentahydroxyhexahydrobenzene are possible, and until a further number of these isomerides are known it is impossible to assign a definite configuration either to d-quercitol or to the new l quercitol.

Aldehydes and Ketones.—The general method for the preparation of aldehydes by the action of organomagnesium haloids on the esters of orthoformic acid dissolved in dry ether (Tschtischabin, *Ber.*, 1904, xxxvii., 186) appears to be applicable to the synthesis of hydro-aromatic aldehydes (*Ber.*, 1904, xxxvii., 850), and in this way hexahydro-m-

* Read before the British Association (Section B), Cambridge Meeting, 1904.

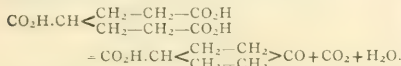
† Report of the Committee, consisting of Dr. E. Divers, F.R.S. (Chairman), Dr. A. W. Crossley (Secretary), Professor W. H. Perkin, F.R.S., Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), Cambridge Meeting, 1904.

toluic aldehyde has been prepared from 3 bromo-1-methyl-hexahydrobenzene.

The preparation of hexahydrobenzyl alcohol has been described by Bouveault (*Comptes Rendus*, 1903, cxxxvii., 60). Methylhexylcarbinol, $C_6H_{11}.CH(CH_3)OH$, is obtained when acetic aldehyde is allowed to act on the magnesium compound of chlorohexahydrobenzene (*Bull. Soc.*, 1903, xxxix., 1049). When these alcohols are oxidised with chromic acid the former yields hexahydrobenzaldehyde and the latter hexahydroacetophenone.

Chloro-derivatives of Ketomethylidihydrobenzene
(Zincke, *Annalen*, 1903, cccxxviii., 261).

Acids.—When pentane- $\gamma\gamma\gamma$ -tricarboxylic acid is digested with acetic anhydride, and then distilled (Perkin, *Journ. Chem. Soc.*, 1904, lxxxv., 416), a remarkable decomposition takes place, with elimination of carbon dioxide and water and formation of δ -ketohexahydrobenzoic acid,—



On reduction the corresponding hydroxy acid is obtained, which yields trans- δ -bromohexahydrobenzoic acid when treated with hydrogen bromide, and this bromo-acid, under the influence of sodium carbonate, gives rise to Δ^1 -tetrahydrobenzoic acid. δ -Ketohexahydrobenzoic acid combines with hydrogen cyanide to form the mixed nitriles of the *cis*- and *trans*-modifications of α -hydroxyhexahydroterephthalic acid. Both the corresponding acids decompose on distillation with formation of Δ^1 -tetrahydroterephthalic acid, identical with the acid synthesised by Baeyer (*Annalen*, 1888, ccxlv., 160).

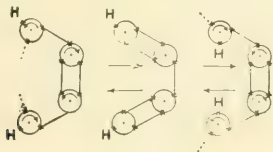


FIG. 1.

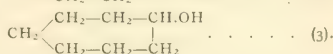
δ -Ketohexahydrobenzoic acid has been used by Perkin (*Journ. Chem. Soc.*, 1904, lxxxv., 654), as the starting point for the synthetical preparation of terpin, inactive terpineol, and dipentene; but as this report does not include a consideration of the terpenes and camphors, an account of this work is not given.

Transformations.—1-Methyl-3-ketohexahydrobenzene has been converted into 1-methyl-2-ketohexahydrobenzene (Wallach, *Annalen*, 1903, cccxxix., 368) by the series of reactions already described (*Reports*, 1903, p. 181).

When 1:5-dimethyl-3-keto- Δ^1 -tetrahydrobenzene (Knoevenagel and Erler, *Ber.*, 1903, xxxvii., 2129) is heated with an equal weight of ammonium carbonate, a small quantity of a base is formed identical with collidine (2:4:6-trimethylpyridine). The mechanism of this process is the exact reverse of Hantzsch's reaction whereby dihydropyridine, under the influence of hydrochloric acid, yields ketotetrahydrobenzene (*Annalen*, 1882, ccxv., 297).

It has been shown by Demjanow and Luschnikov (*Cent. Blatt.*, 1903, [1], 828) that it is possible to convert a substance containing a tetramethylene ring into one containing a pentamethylene ring (cyclopentanol from tetramethylenemethylamine); and, in continuance of this work, Demjanow has now provided an example of the conversion of a ring containing six carbon atoms into one containing seven (*Cent. Blatt.*, 1904, [1], 1214). On distilling hexahydrobenzamide with phosphorus pentoxide it yields cyanohexahydrobenzene (1), which on reduction gives the corresponding amine (2). When the hydro-

chloride of this amine is acted on with silver nitrite it is converted into an alcohol identical in every respect with suberyl alcohol (3), already described by Markownikoff (*Ber.*, 1893, xxvi., R, 813).



A study of the action of bromine on 3:5-dichloro-1:1-dimethyl- Δ^2 :4-dihydrobenzene (Crossley, *Journ. Chem. Soc.*, 1904, lxxxv., 264) has shown that the resulting hydro-aromatic bodies very readily lose hydrogen bromide to form aromatic substances, of which the two principal ones are 3:5-dichloro-4-bromo-*o*-xylene and 3:5-dichloro-6-bromo-*o*-xylene. Since the dichlorodimethylidihydrobenzene, which forms the starting-point of the research, contains the *gem*-dimethyl group, the migration of one of these methyl groups becomes an essential step in the production of an aromatic compound. The reaction has therefore been worked out so as to gain an insight into the course of such changes, more especially as, on account of the symmetry of the molecule, it forms one of the simplest cases in which the wandering of an alkyl group can take place. The reaction is largely influenced by the condition of experiment, but no substance has been encountered in which an alkyl group has wandered into any but an ortho-position.

The Nature of Double Linkings.—Recent experimental work has enriched our knowledge of the behaviour of

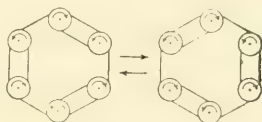


FIG. 2.

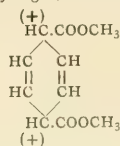
substances containing double linkings, more especially as regards the property of addition. In the case of a substance containing several double bonds in the molecule, these bonds often do not behave independently of one another. Thiele's theory (*Annalen*, 1899, cccvi., 87) of partial valencies provides a possible explanation of many such cases. Knoevenagel (*Ber.*, 1903, xxxvii., 2803) considers it essential to study the movement of the atoms themselves in the molecule, and assumes that doubly linked carbon atoms are in a continuous state of oscillatory motion. In the case of a substance, such as butadiene, the formation of the dibromide $BrCH_2-CH=CH-CH_2Br$ is explained by supposing the swinging motion of the carbon atoms to be taking place first in one direction and then in the opposite, as indicated in the accompanying diagram (Fig. 1).

Continuous motion in one direction only is prevented by the hydrogen atoms attached to the terminal carbon atoms, which come into the plane of rotation. It is quite another matter in the case of benzene, where alternate carbon atoms are supposed to rotate continuously in opposite directions, because none of the valencies which pass into the plane of rotation have hydrogen atoms attached to them; the result is that the double linkings change their position and travel round the ring (Fig. 2).

Such a theory indicates the possibility of new types of isomerism, more subtle even than optical isomerism, and it is pointed out that cases of supposed polymorphism, e.g., the quinols and benzophenone, may be in reality mani-

festations of structural differences of the above type. Knoevenagel supports Lehmann's view ("Molekularphysik," ii., 413), that substances exhibiting difference in crystalline form afford evidence of difference in chemical or, perhaps better, physical constitution.

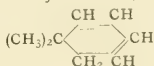
It is also suggested that bodies of the type of ethyl $\Delta^2:5$ -dihydroterephthalate should be particularly liable to lose a molecule of hydrogen, since the two hydrogen atoms



marked (+) would be in a continuous state of bombardment, due to the swinging motion of the carbon atoms connected by a double bond. On increasing the temperature this state of things would become sufficiently intense to cause the partial dissociation of the molecule with evolution of hydrogen. This actually happens in the case of the above ethereal salt on heating (*Ber.*, 1903, xxxvi., 2857) in an atmosphere of carbon dioxide, especially in presence of platinum black. The evolved hydrogen is much smaller in amount than required by theory, only 18 c.c. being obtained by heating 1 grm. of the salt instead of 113 c.c. This is readily explained, for the evolved hydrogen combines with some unaltered ester, and the result of the reaction is the production of methyl terephthalate and methyl hexahydroterephthalate.

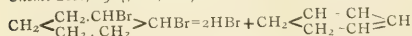
$\Delta^1:3$ -DIHYDROBENZENE. By Dr. A. W. CROSSLEY.

In the last report of this committee (Southport, 1903, p. 182) brief allusion was made to the preparation of $\Delta^1:3$ -dihydrobenzene; work in this direction has now been completed, with results which entirely confirm the preliminary experiments. The hydrocarbon obtained from dimethyldihydroresorcin by Crossley and Le Sueur (*Journ. Chem. Soc.*, 1902, lxxxi., 822) was proved to be 1:1-dimethyl- $\Delta^2:4$ dihydrobenzene, and by submitting



dihydroresorcin to an identical series of reactions a hydrocarbon was obtained (Crossley and Haas, *Journ. Chem. Soc.*, 1903, lxxxi., 494), which differed from any previously prepared dihydrobenzene in only combining with one molecule of bromine to give a dibromodihydrobenzene melting at 104.5°. It was therefore suggested that the double bonds would be in the position 1:3, and the hydrocarbon prepared by Baeyer (*Annalen*, 1894, cclxxviii., 88) and Markownikoff (*Annalen*, 1898, ccxii., 29) would be $\Delta^1:4$ -dihydrobenzene, which is characterised by directly adding on four atoms of bromine to form a solid tetrabromide melting at 184°. Harries and Antoni (*Annalen*, 1903, cccxxviii., 102) consider that their work proves this suggestion to be incorrect.

Unfortunately it was not found possible to prepare pure $\Delta^1:3$ -dihydrobenzene from dihydroresorcin, but this end has now been attained by the removal of the elements of hydrogen bromide from dibromotetrahydrobenzene (*Proc. Chem. Soc.*, 1904, xx., 160):—



The reaction can only take place in one way, and therefore leaves no doubt as to the constitution of the resulting hydrocarbon, which like that obtained from dihydroresorcin only adds on two atoms of bromine to give a solid melting at 104.5°. That this latter substance is in reality a dibromodihydrobenzene is conclusively proved by the fact

that on treatment with quinoline it loses two molecules of hydrogen bromide, yielding benzene.

It seems indisputable that, as already suggested, the hydrocarbon obtained from dihydroresorcin or from dibromotetrahydrobenzene is $\Delta^1:3$ -dihydrobenzene, and the hydrocarbon giving the tetrabromide melting at 184° must therefore be $\Delta^1:4$ -dihydrobenzene.

ON ACTIVE CHLORINE.*

(PRELIMINARY NOTE).

By D. L. CHAPMAN and C. H. BURGESS.

We much regret that the necessity to be brief prevents us from referring to the work of others as we should like, and also from entering into any experimental details connected with our own work, or even from explaining fully the views which we hold, on this subject and on subjects closely allied to it. We hope, however, to be able to show that some of the theories which have been proposed to account for the phenomenon known as the induction period cannot be reconciled with the newly discovered facts, and that the theories in question will have to be modified, perhaps to the extent of admitting new conceptions into the science. It will be best now to describe, leaving any criticism until later, those theories which account both for the induction period and for the catalytic action of water.

The theories in question postulate the gradual formation of an intermediate compound as the result of the interaction of one or both of the reacting substances with the catalyser. Since the intermediate compound may be conceived as differing in its mode of action it will be convenient to adopt a rough classification.

In the first place, it may be assumed that the compound is formed and subsequently destroyed; for example, it may be supposed that the changes which take place are represented by the equations:—

- I. $\begin{cases} a. \text{H}_2\text{O} + \text{Cl}_2 = \text{H}_2\text{O} \cdot \text{Cl}_2. \\ b. \text{H}_2\text{O} \cdot \text{Cl}_2 + \text{H}_2 = \text{H}_2\text{O} + 2\text{HCl}. \end{cases}$
- II. $\begin{cases} a. \text{H}_2\text{O} + \text{Cl}_2 = \text{HCl} + \text{HClO}. \\ b. \text{HCl} + \text{HClO} + \text{H}_2 = 2\text{HCl} + \text{H}_2\text{O}. \end{cases}$
- III. $\begin{cases} a. \text{Cl}_2 + \text{H}_2\text{O} = \text{Cl}_2\text{O} + \text{H}_2. \\ b. \text{Cl}_2\text{O} + 2\text{H}_2 = 4\text{HCl} + \text{H}_2\text{O}. \end{cases}$
- IV. $\begin{cases} a. \text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{O (nascent)}. \\ b. \text{O (nascent)} + \text{H}_2 + 2\text{HCl} = 2\text{HCl} + \text{H}_2\text{O}. \end{cases}$

Of these theories I. and III. are excluded by direct experiment, since it has been shown that an induction period still occurs even after the introduction of chlorine monoxide or hypochlorous acid into the system.

In the second place, it may be supposed that the intermediate compound is not destroyed, but that it simply acts as a catalyser in the presence of which the combination of the hydrogen and chlorine can more readily take place. The actions represented by the equations below is an example of this:—

$$\text{V. } \begin{cases} a. \frac{n}{m} \text{H}_2\text{O} + m \text{Cl}_2 = (\text{H}_2\text{O})_n \text{Cl}_{2m}. \\ (\text{H}_2\text{O})_n \text{Cl}_{2m} + \text{Cl}_2 = \text{Cl}_2 \{ (\text{H}_2\text{O})_n \text{Cl}_{2m} \}. \\ \text{Cl}_2 \{ (\text{H}_2\text{O})_n \text{Cl}_{2m} \} + \text{H}_2 = 2\text{HCl} + \{ (\text{H}_2\text{O})_n \text{Cl}_{2m} \}. \end{cases}$$

Leaving for the present the consideration of these two classes of hypothesis, I will describe some experiments which have been selected as illustrations.

Experiments on the Influence Exerted by the Liquid contained in the Actinometer.

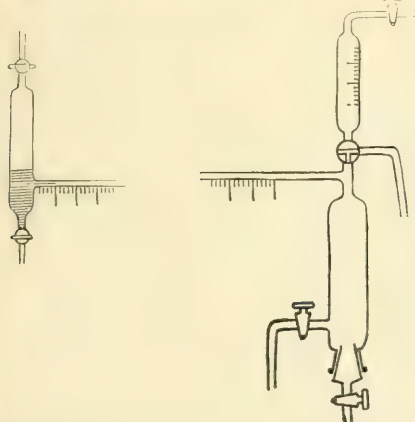
The actinometer was a modification of the one used by Bunsen and Roscoe, and is shown in Fig. 1. Measured quantities of liquid or gas can be introduced at any time. The capacity of the bulb was 70 c.c., and the length of the index about 1 metre. For comparative experiments almost

* Read before the British Association (Section B), Cambridge Meeting, 1904.

precisely similar actinometers made from the same glass were used.

If such an apparatus containing electrolytic gas and a little water is exposed to light, there is for some time after it is first exposed no appreciable movement of the index. Then a slight movement is observed, which increases rapidly until a maximum and constant rate is attained. The time from the first exposure to light to the attainment of the constant rate has been named by Bunsen and Roscoe the induction period. It was accidentally discovered that if after this stage is reached the actinometer be removed from the bath, thoroughly shaken in the dark, and re-exposed to light, a new induction period is observed, which is, however, not so long as the first period. The same operation may be repeated with the same result, namely, there is each time a fresh induction period which is always shorter than the one immediately preceding. The numbers below are the lengths of the successive induction periods in an experiment of this kind.

Periods	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Minutes	28	18	13	12	12	8	6	5	3	1



The same phenomenon was observed when the actinometer contained acid or saline solutions in the place of water.

The explanation of the foregoing results is obvious. By the action of light on the moist mixture of hydrogen and chlorine they acquire the power of combining more readily with one another, or, concisely, they become active. The power of combining more easily, or the *activity*, is removed when the gases are shaken with the water contained in the actinometer, but in time this water becomes saturated with activity, and when this is the case it is no longer able to render the mixed gases inactive.* The best method, therefore, of inducing the gases is to expose them frequently to light, and then to shake them with the liquid contained in the vessel. If the gases are thoroughly induced in this way a sudden exposure to even a weak light is accompanied by a sudden expansion. This expansion with a weak light can be used as a test of the thoroughness of the insulation of the mixture.

There are several peculiarities connected with the absorption of the activity by various liquids, and also with the rate of decay of the activity, which must be left until a fuller account of the work can be given.

* As I shall frequently have to refer to a liquid in this condition, it will simply be described as an active liquid.

There is another relation which, although it is not connected with the main argument, is of importance in connection with the right interpretation of many experiments, namely, the influence of small quantities of air on the length of the induction period. Bunsen and Roscoe have shown that the addition of small quantities of air decrease in a remarkable degree the sensitiveness of electrolytic gas. Does it increase the length of exposure to a given light required to make the gas active? To test this, two similar actinometers were filled with the same gas mixture, and after a small quantity of air had been added to one they were both exposed to the same light. The experiment was then repeated, exchanging the actinometers. The results are recorded below:—

Experiment I.

Induction period.	Sensitiveness.
= 35 mins.	= 12.8 c.m. per min.
= 30 "	= 2.85 " "

Experiment II.

Induction period.	Sensitiveness.
= 55 mins.	= 9.9 c.m. per min.
= 46 "	= 2.2 " "

So that the presence of air certainly does not lengthen the induction period.

The Activity is due to the Condition of the Chlorine.

Having obtained the necessary information concerning the part played by the liquid in the actinometer, it became a simple matter to find out how far the chlorine is responsible for the induction period.

F. V. Bevan (*Phil. Trans.*, ccii., pp. 71—121) has recently shown that previous exposure of chlorine to light produces an increase in the rate of action, when the chlorine is mixed with hydrogen and exposed to light; but the important part played by the liquid in contact with the mixed gases was not at the time that these experiments were performed generally recognised. The difference observed by him with insulated and uninsulated chlorine was not sufficient to justify the conclusion that the main fact to be taken into account in explaining the induction period was the condition of the chlorine. Experiments performed by us in which care was taken to thoroughly induce both the chlorine and the liquid in contact with it have shown that the induction period is due to the condition of the chlorine. The results obtained in one experiment are given below. The same light was employed in both cases, and the readings were taken every two minutes.

Hydrogen + insulated chlorine.			Hydrogen + uninsulated chlorine.
Time.	Reading.	Difference.	
2 h. 2 m.	18.5	—	Induction period = 50 mins.
2 " 4 "	25.5	7.00	
2 " 6 "	35.4	9.90	
2 " 8 "	45.2	9.80	
	&c.	&c.	
The induction period = a few seconds.			
Sensitiveness = 9.80.			

Methods by which the Chlorine and its Solution can be made Active.

It has been shown that chlorine gas can be made active—

- By exposure to light.
 - By heating to a temperature of 100° C. and then cooling.
 - By the silent discharge.
- And that a solution of chlorine can be made active—
- By exposure to light.
 - By heating to 100° C.
 - By contact with active chlorine.

On the Solubility of the Activity.

The power possessed by saline and acid solutions of removing the activity from chlorine is greater than that possessed by water. No attempt has been made to measure exactly the specific absorbing power of the solution

in question, but roughly with a saturated solution of barium chloride this power is about four times as great as with pure water. The increased solubility of the activity in saline solutions proves that the salt is itself capable of absorbing the activity or of rendering the water in which it is dissolved more capable of doing so. The following experiment proves the former alternative to be correct:—Chlorine gas was shaken for about half-an-hour with a saturated aqueous solution of barium chloride in the daylight. The chlorine was then removed by evacuating the apparatus, and the water was distilled off, leaving dry crystals of barium chloride. These barium chloride crystals were immediately dissolved in an active solution of chlorine in water. A solution of practically the same strength was made by dissolving ordinary crystallised barium chloride in another portion of the active chlorine solution. The two solutions prepared in the way described were then introduced into two similar actinometers containing electrolytic gas, and the actinometers were exposed to the same light. With the actinometer which contained ordinary barium chloride, the induction period was several hours, whereas with the other it was only a few minutes. So that barium chloride can exist both in an active and in an inactive condition.

The following facts have also been experimentally demonstrated:—

1. An active aqueous solution exposed to the air in an open vessel becomes inactive exceedingly slowly.
2. Active crystals of barium chloride behave in precisely the same way as ordinary barium chloride on exposure to air for a few hours, showing that they rapidly lose their activity.
3. An active solution of chlorine either in water or in a saline solution is still active after the chlorine has been removed in a vacuum.

The Intermediate Compound Hypothesis.

Returning now to a brief consideration of the intermediate compound hypothesis, we have already seen that the reaction cannot be conceived as proceeding according to the Equations II. and III.

The assumption that the reaction proceeds according to Equation IV. is inadmissible, since it will not account for the well established induction period, which has been observed by Harden and others with a mixture of carbon monoxide and chlorine.

Equations I. and V. therefore remain as possible methods of representing the changes which take place.

The objections to I. are grounded upon relative measurements made by us of the induction period and the sensitiveness.* It has been shown that in certain circumstances the induction period becomes so long that if combination were proceeding at the ultimately attained maximum rate during the same period of time, all the electrolytic gas in the actinometer would be converted into hydrochloric acid; a result which—taken in conjunction with the law of mass—proves that all the chlorine must have been converted into the compound $\text{Cl}_2 \cdot \text{H}_2\text{O}$ before hydrochloric acid began to be formed in appreciable quantity, and this without a notable change in volume. This is in itself sufficient ground for definitely rejecting the hypothesis in question.

The objections which can be raised against a theory which postulates the formation of a catalyser of the type given under Equation V. appear to be equally conclusive.

Bunsen and Roscoe have shown, and their results have been confirmed and extended by us, that admixture of inactive with active electrolytic gas results in a mixture in which practically no combination occurs on exposure to light, but the effective action of the catalyser should be proportional to its amount—if it is not, it ceases to be by itself a satisfactory explanation. We have shown in a separate series of experiments, that reduction of pressure must result in reducing the amount of this hypothetical catalyser does not cause a new induction period.

It is difficult to avoid the conclusion that the exposure of moist chlorine to light results in the augmentation of a physical quantity closely analogous to a potential or a temperature. A mixture of active with inactive chlorine assumes, after a short time, the mean potential of the two gases, and combination with hydrogen will not take place on exposure to light. Reduction of pressure does not alter the potential, and combination with hydrogen will take place immediately under the same conditions. How such an hypothesis can be reconciled with the known facts of water catalysis must be left until a fuller account of the work can be given.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1904.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, September 10th, 1904.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 203 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Aug. 2nd to Aug. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 203 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford has been fairly well distributed throughout the month, and rain has fallen on nine days. The total amount recorded is 1.61 inches, and the average for August is 2.38 inches; we have, therefore, a deficit of 0.77 inch, which, if subtracted from the previous excess of 2.23 inches, leaves a total excess for the year of 1.46 inches, or 9.3 per cent above the thirty-five years' average.

Our bacteriological examinations of 384 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 382 others from special wells, standpipes, &c., making 766 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	142
New River, filtered (mean of 78 samples) ..	5
Thames, unfiltered (mean of 26 samples) ..	988
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 205 samples) ..	22
Ditto ditto highest	372
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	231
River Lea, from the East London District clear-water wells (mean of 26 samples) ..	7

Of the 300 daily samples taken from the general filter wells of the Metropolitan Water Board, eighteen samples, or 5.8 per cent, were sterile. Eleven samples, or 3.5 per cent, contained more than 100 microbes, and of these eight samples contained more than 150 microbes per c.c.

* By the sensitiveness is to be understood the rate of combination of the hydrogen and chlorine after the induction period is over.

The eleven excess samples contained an average of 186 microbes per c.c. In July seven excess samples contained an average of 177 microbes per c.c.

The above results show that the recent high degree of purity of the London waters has been well maintained during the month of August.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

NOTICES OF BOOKS

Kritische Studien über die Vorgänge der Autoxydation.
("Critical Studies on the Processes of Autoxidation").
By C. ENGLER and J. WEISSBERG. Braunschweig:
Friedrich Vieweg und Sohn. 1904.

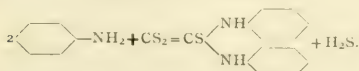
By the help of this monograph investigators engaged in researches on questions relating to this particular branch of chemistry will get much assistance in estimating the meaning and importance of any results they may have obtained. The book gives a critical review of the facts which have been amassed on this subject, and examines the often contradictory theories which have been put forward. The authors apply the theory of autoxidation to the interpretation of many cases, which he divides into two well differentiated classes, described as direct and indirect processes respectively, and after sections on autocatalysis and the effects of the presence of various chemical substances and physical conditions on autoxidation, he passes to the consideration of the part played by oxygen in the living organism, and to a very restricted review of the phenomena exhibited by the oxidases. In view of the comparative neglect which the theory of autoxidation processes has suffered, as seen by the lack of authoritative text-books on the subject, though numerous isolated investigations have been conducted on it, it will probably be found that this small book will supply a want.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 8, August 22, 1904.

Examination and Synthetic Preparation of certain Symmetric Cyclic Thiourides.—Emm. Pozzi-Escot.—The cyclic thiourides can be easily obtained by the action of the cyclic amines on carbon disulphide in presence of a desulphurating agent. If the amines are merely placed in contact with the carbon disulphide nothing is produced, even at the boiling-point of the mixture. It is necessary, in order to obtain good results, to dissolve the amine and the carbon disulphide in suitable solvents, and to operate in presence of a desulphurating agent. The best solvent is found to be alcohol, and the best desulphurators the caustic alkalis. The general reaction of formation is—



No. 9, August 29, 1904.

This number contains no chemical matter.

A Selection from MACMILLAN & CO.'S BOOKS FOR STUDENTS OF CHEMISTRY.

THIRD EDITION. Entirely Rewritten and Enlarged
**CHEMICAL TECHNOLOGY AND ANALYSIS OF
OILS, FATS, AND WAXES.**

By Dr. J. LEWKOWITSCH, M.A., F.I.C., &c.
With 88 Illustrations and numerous Tables. Medium 8vo, gut tops.

NATURE.—"The standard English book of reference on the subject."

SECOND EDITION.

TABLES FOR QUALITATIVE CHEMICAL ANALYSIS.

Arranged for the Use of Students.
By A. LIVERSIDGE, M.A., LL.D., F.R.S., Hon. F.R.S.E.;
Associate of the Royal School of Mines, London; Professor of
Chemistry in the University of Sydney.
Super Royal 8vo., 4s. 6d. net.

PHARMACEUTICAL JOURNAL.—"The tests given by the author have been well selected, and the matter is clearly arranged. . . . Any student who buys this work will find that he has a helpful and clear guide to the processes of qualitative chemical analysis."

FRACTIONAL DISTILLATION. By
SYDNEY YOUNG, D.Sc., F.R.S., Professor of Chemistry in University College, Bristol. With 72 Illustrations. Crown 8vo, 8s. 6d.

**AN INTRODUCTION TO THE STUDY OF
CHEMISTRY.** By Prof. W. H. PERKIN, JR., Ph.D., F.R.S.,
and R. VAN LEAN, D.Sc., B.A. (Lond.). Globe 8vo, 2s. 6d.

A PRIMER OF CHEMISTRY. By Sir
HENRY E. ROSCOE, F.R.S. Illustrated. With Questions.
Fifth 8vo, 1s.

**INORGANIC CHEMISTRY for BEGIN-
NERS.** By Sir HENRY E. ROSCOE, F.R.S. Assisted by
JOSEPH LUNT, B.Sc. Globe 8vo, 2s. 6d.

**LESSONS in ELEMENTARY CHEMIS-
TRY, INORGANIC and ORGANIC.** By Sir H. E. ROSCOE,
F.R.S. Sixth Edition, thoroughly revised. Fcap. 8vo, 4s. 6d.

**INORGANIC CHEMISTRY FOR AD-
VANCED STUDENTS.** By Sir H. E. ROSCOE, F.R.S., and
Dr. A. HARDEN. Globe 8vo, 4s. 6d.

A TREATISE ON CHEMISTRY. By Sir
H. E. ROSCOE, F.R.S., and the late C. SCHORLEMMER,
F.R.S. Completely revised by Sir H. E. Roscoe, assisted by
Drs. H. G. COLMAN and A. HARDEN. 8vo. Vol. I. The Non-
Metallic Elements. 21s. Vol. II. The Metals. 31s. 6d.
Vol. III. The Chemistry of the Hydrocarbons and their Deriva-
tives, or Organic Chemistry. Parts II., IV., and VI., 21s. each.
Part III., 18s.

**INTRODUCTORY CHEMISTRY FOR
INTERMEDIATE SCHOOLS.** By L. M. JONES, B.Sc.
Globe 8vo, 2s.

**CHEMISTRY FOR ORGANISED
SCHOOLS OF SCIENCE.** By S. PARRISH, B.Sc. With
Introduction by Dr. FORSTER. Globe 8vo, 2s. 6d.

**PRACTICAL INORGANIC CHEMIS-
TRY.** By G. S. TURPIN, D.Sc. Globe 8vo, 2s. 6d.

LESSONS in ORGANIC CHEMISTRY.
By G. S. TURPIN, D.Sc. 2s. 6d.

**A TEXT-BOOK of INORGANIC CHE-
MISTRY.** By Prof. IKA REMSEN. 8vo, 16s.

INORGANIC CHEMISTRY. By Prof. I.
REMSEN. Crown 8vo, 6s. 6d.

ORGANIC CHEMISTRY. By Prof. I.
REMSEN. Crown 8vo, 6s. 6d.

The ELEMENTS of CHEMISTRY. By
Prof. I. REMSEN. 11th Impression. Fcap. 8vo, 2s. 6d.

**COLLEGE TEXT-BOOK of CHEMIS-
TRY.** By Prof. I. REMSEN. Extra Crown 8vo, 8s. 6d. net.

MACMILLAN & CO., Ltd., LONDON.

THE SIR JOHN CASS TECHNICAL INSTITUTE. JEWRY STREET, ALDGATE, E.C.

Principal—CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.

EVENING CLASSES IN CHEMISTRY, METALLURGY, PHYSICS, and MATHEMATICS.

Designed to meet the requirements of those engaged in CHEMICAL, METALLURGICAL, and ELECTRICAL INDUSTRIES, and in trades associated therewith.

Also preparation for the B.Sc. Examination of London University. Every facility for Special and Advanced Practical Work in well-equipped Laboratories, both in the Afternoon and Evening

CHEMISTRY		{ CHARLES A. KOHN, M.Sc., Ph.D., F.I.C.
PHYSICS		R. S. WILLOWS, D.Sc., M.A.
METALLURGY		C. O. BANNISTER, Assoc.R.S.M.
MATHEMATICS		G. M. K. LEGGETT, B.A.

CLASSES IN METALLURGY.

GENERAL METALLURGY.

THE METALLURGY OF GOLD, SILVER, and LEAD.

FUEL and REFRACTORIAL MATERIALS.

METALLOGRAPHY, including PYROMETRIC WORK.

ASSAYING.

ANALYTICAL CHEMISTRY,

Including ELECTROLYTIC and GAS ANALYSIS.

Each Course of Lectures will be accompanied by suitable Laboratory Work.

GLASS BLOWING.

A series of Courses of Instruction will be given during the Session by Mr. A. C. COSSOR.

SESSION began MONDAY, SEPTEMBER 26th.

The Institute is readily accessible, and near to Fenchurch Street, Liverpool Street, Broad Street, and Metropolitan Railway Stations. For details of the Classes apply at the Office of the Institute, or by letter to the PRINCIPAL.

W. H. DAVISON, M.A.,
Clerk to the Governing Body.

THE POLYTECHNIC,

309, REGENT STREET, W.

UNIVERSITY OF LONDON PREPARATION CLASSES.

Full Courses of Instruction for Matriculation,

Inter, Arts, Science, and Engineering, and Final Arts. Special Courses for Final B.Sc. in Mathematics, Physics, and Chemistry.

Examinations are held at the above Institute.

TERM commenced SEPTEMBER 16th, 1904.

Courses are so arranged that Students can do the work on Saturday and one evening per week.

Full particulars can be obtained on application to the DIRECTOR OF EDUCATION.

MICA

Telephone
No. 2248
Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., & London
103, MICA MERCHANTS.

Manufacturers of Mica Goods or Electrical and ALL purposes.
Contractors to His Majesty's Government.

To Chemical Manufacturers, Iron and Metal Merchants, and others.—Messrs.

FULLER, HORSEY, SONS, and CASSELL

are instructed to SELL by AUCTION, at the Lea Chemical Works, Carpenters' Road, Hackney Wick, on THURSDAY, Oct. 20, at Eleven o'clock precisely.

CHEMICAL PLANT and MACHINERY.

including about 80 tons of lead in tanks, coolers, vats, &c., enamelled iron baths, two pairs vacuum pumps, Johnson's air compressor, seven steam and other pumps, quantity lead and enamelled iron trays, pair of edge runners, three acid grinding mills, three sifters, two ranges of coke oven, disintegrator, water softening apparatus, large quantity of tin, lead, and iron piping and cocks, aluminium trays, three w.i. water tanks up to 3000 gallons, about 30 tons c.i. floor plates, Tangyes' 17-h.p. horizontal steam engine, three smaller steam engines, two Lancashire boilers, 7 ft. and 7 ft. 6 in. diameter, 30 ft. long, two electric boilers, shafting and belting, steam winch, crab, 10 cwt. weighing machine, 7½ in. centre screw cutting lathe, four cranes, blocks, and chain, quantity stores and material, office furniture, and Effects.—May be viewed and catalogues had of Messrs. KINGSFORD and DRAKE, Solicitors, Bank Street, Ashford, Kent; and of Messrs. FULLER, HORSEY, SONS, and CASSELL, 11, Billiter Square, E.C.

SECOND EDITION, NOW READY.

With Illustrations.

Price 2s. net (post free 2s. 1½d.)

Mdme. CURIE'S Thesis

ON

RADIO-ACTIVE SUBSTANCES.

REPRINTED from the CHEMICAL NEWS.

CONTENTS.

Introduction.—Historical.—Chap. I. Radio-activity of Uranium and Thorium; Radio-active Minerals.—Chap. II. Method of Research.—Chap. III. Radiation of the New Radio-active Substances.—Chap. IV. Communication of Radio-activity to Substances Initially Inactive.—Nature and Cause of the Phenomena of Radio-activity.

16, NEWCASTLE ST., FARRINGTON ST., E.C.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

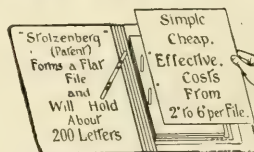
Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

Perfect Order amongst your Scientific Papers, Research Records, &c.,

IS SECURED BY THE

"STOLZENBERG" SYSTEM OF FILING.



The "Unit" of the System is a simple Flat File, made in six distinct colours, for classifying under Subjects, &c.

Used by SIR WILLIAM CROOKES, LORD KELVIN, Royal Commission on Tuberculosis, Baden Aniline Works (50,000), and by thousands of private persons as well as Business Concerns.

Satisfaction guaranteed; otherwise goods taken back and money returned.

Sample Set, consisting of 12 best Files, 4to and 8cp., with strong nickel-plated Perforator, and Patent Lifter, packed in leather-board box, 10/6 post free.

THE STOLZENBERG PATENT FILE CO.,
50, Bishopsgate St. Without, London, E.C.

THE CHEMICAL NEWS.

VOL. XC., No. 2341.

ON A METHOD OF REPRESENTING THE PROPERTIES OF ELEMENTS GRAPHICALLY BY MEANS OF CHARACTERISTIC SURFACES.

(PRELIMINARY NOTE).

By GEOFFREY MARTIN, B.Sc.

EVERY relationship which the human mind is capable of comprehending can be represented geometrically in some way or other.

If this relationship takes a form capable of being referred to number, or subjected to measurement, then it can be represented geometrically by a figure whose magnitude and shape measures numerically the degree of the relationship.

And since every geometrical locus is capable of being represented by an analytical expression, it follows that every relationship which the human mind is capable of comprehending is ultimately expressible by means of the symbols of a mathematical calculus.

In particular, the properties of an element are also relationships which are capable of being, in some way or other, portrayed geometrically.

And since these properties are, in general, subjectible to measurement, they must also be capable of being expressed quantitatively by means of an analytical expression which is the equation of the geometrical figure which pictures them.

The general problem which we propose to investigate is the construction of some geometrical figure which will quantitatively portray the chemical properties of an element.

So that to every different element there will correspond a different figure; and by merely inspecting the shape of the figure corresponding to a particular element when viewed under particular conditions of temperature and pressure, we will be able to predict quantitatively beforehand the effects the element will produce.

The equation of this figure will, in fact, bear the same relationship to that manifold of properties which is comprehended under the name of the element, as the equation of a curve bears to that manifold of geometrical points which is comprehended under the name of the curve. For just as in the former case all the geometrical properties of the curve can be deduced from the analytical expression which represents it, so in the former case all the chemical properties of an element can be deduced from the analytical expression of the geometrical locus which represents it.

In order to do this we must first determine upon what factors depend the chemical properties of an element; and then we must devise some method of representing these factors geometrically.

Now it can be proved *rigorously*—though the proof is too long to give here—that the way an element reacts depends entirely upon the forces with which it attracts other elementary atomic species. So that, knowing these forces, we know all the chemical peculiarities of the element. These are, in fact, the forces which decide with which elements a given element will combine, its degree of chemical activity, the stability of the compounds it produces, and (as I have already pointed out in the *CHEMICAL NEWS* for May 20, 1904, p. 241), to a very great extent the fusibility, volatility, solubility, hardness, &c., of the element itself and of the compounds it produces.

If, therefore, we can devise a geometrical surface which will represent the magnitude and relative intensity of the

affinities of an element, this surface may be called the *characteristic surface* of the element, since from it can be deduced all the characteristic properties of the element.

Now such a characteristic surface may be constructed for any given element in the following way:—

Let the Periodic System of the elements be plotted out on a flat surface as base as follows:—

The group numbers are plotted along o X, and the series numbers along o Y (Fig. 1).

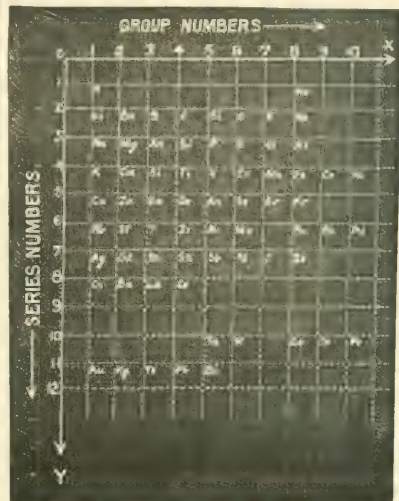


FIG. 1.—Showing how the Position of an Element in the Periodic System is fixed by its X and Y co-ordinates, X being the Group Number, and Y the Series Number.

Then any element in the Periodic System may be denoted by a point, which is completely known when its x and y co-ordinates are known. For example, the point $x = 1, y = 2$ represents Li; $x = 5, y = 6$ represents niobium; $x = 4, y = 4$ represents Ti (see Fig. 1).

Suppose now we take any given atomic species A, whose characteristic surface it is required to construct, and measure the attractive force which it exerts on the atoms of the various elements of the Periodic System. And let us erect a perpendicular from every point in the previous diagram of a length proportional to the attractive force which A exerts on the element represented by the point.

Now imagine a surface to be described through the summits of these perpendiculars. Then this surface is the characteristic surface of the atomic species A, and can be expressed by an equation in three variables (z being the magnitude of the attractive force, $F(x, y, z) = 0$, and from this equation can be deduced (by given successive integer values to x and y) all the different affinities of the element A.

Hence, from the equation $F(x, y, z) = 0$ can be deduced all the chemical properties of the element. Moreover, the variations with the temperature, &c., in the intensities of these chemical forces will be expressed by variations in the shape of the characteristic surface. So that all the changes in the properties of an element, with the temperature, &c., can be followed by studying the changes in the shape of its characteristic surface.

The characteristic surface of an element, however, is not so simple as the above discussion might lead one to suppose. For every different element can assume a number of different valency states, in each of which it exerts a different attractive force on any given element. So that to each different valency state assumable by an element there will correspond a different affinity surface, and the collection of these different affinity surfaces may be comprised under the name of the "characteristic surface" of the element. Making, however, the assumption that any and every element can assume every grade of valence between 1 and 8—those grades of valence known to us being regarded as simply those which the element attains a condition of greatest repose or chemical equilibrium when viewed under the conditions of temperature and pressure under which we live and work, the other grades being as yet unknown—it can be shown that the total number of affinity surfaces can, by a suitable artifice, be reduced to 64, and the complete analytical expression of this collection of affinity surfaces presents a complete picture of all the chemical, and a fairly complete picture of the physical, properties of the element and its compounds, indicating, for example, precisely the relative stability of the different valency compounds it enters into with any element x, y ; how it will react, with what elements it will combine, and whether the compounds thus produced are stable or not; whether the element is metallic or non-metallic in properties, &c.

I have worked out completely the theory of these surfaces, but the method is too long to be indicated here, but will be published with the complete memoir.

There is, however, one affinity surface which is of peculiar interest, namely, that belonging to a given element when it and all the other elements of the periodic system are in that valency state in which they, under ordinary conditions of temperature or pressure, attain a condition of greatest chemical repose or equilibrium.

I have constructed such affinity surfaces (considering the element of the odd series) for the following elements:—H, Li, Na, K, Cu, Ag, Au; Mg, Zn, Cd, Hg; B, Al, Ti, C, Si, Sn, Pb; N, P, As, Sb, Bi; O, S, Se, Te; F, Cl, Br, I; and have obtained some remarkable results, which may be briefly summed up thus:—

1. The affinity surfaces of chemically similar elements are of a similar shape, and those of chemically unlike elements of a dissimilar shape—as is demanded by the theory of chemical similar elements.
2. The form of the affinity surface of a metal is diametrically opposite to that of a non-metal.

When we study the affinity surfaces of a series of elements (such as Li, Be, B, C, N, O, F, or N, P, As, Sb, Bi), which pass from a metallic to a non-metallic condition, we find that the passage of *metals* into *non-metals* is attended by a transformation of the shape of the affinity surface from the form of an irregular wave surface which has its crest over the later groups of the Periodic System (such as O and the halogen elements) into a wave surface which has its crest over elements of the early groups of the Periodic System (such as the alkali and alkaline earth metals).

And that elements of intermediate properties possess affinity surfaces of shapes intermediate between those of pronounced metals and pronounced non-metals.

The affinity surfaces of Li, Na, K are of nearly the same shape as the affinity surfaces of F, Cl, Br; except that they bear to them the same relationship that the image of an object in a mirror bears to the object—the surfaces for Li, Na, K being "right-handed"; those of F, Cl, Br are "left-handed."

3. The chemical inactivity of nitrogen is to a great extent only an apparent effect.

A study of the affinity surface of nitrogen shows that it possesses chemical affinities of a strength almost comparable to those of Na or Cl, only it differs from these elements as regards the element it exerts them on.

Thus, K expends its energies upon elements belonging to

the later groups of the Periodic System (viz., O, S, Se, and F, Cl, Br, I), but has little affinity for elements of the earlier groups (such as the alkali metals and alkaline earth metals). And *chlorine* expends its energies principally upon elements of the early groups of the Periodic System (such as the alkali metals and alkaline earth metals), but has little affinity for elements of later groups (such as O, S, Se, F, Cl, Br, I).

Nitrogen, on the other hand, expends its energies on elements of intermediate groups—principally those of Groups III., IV., and V.—but has little affinity for those of earlier or later groups (such as the alkali elements and the halogens).

For example, its combinations with boron, silicon, and phosphorus are quite remarkable by reason of their great stability—the phosphide P_3N_5 , for instance, must be heated in O gas to a temperature above that at which hard glass melts, *before* the oxygen begins to act on it!

The current belief that nitrogen is an element characterised by its chemical inertness, and by the feebleness of its chemical affinities, is therefore not entirely correct.

Cl and K appear to us to be ever so much more chemically active than nitrogen, principally because they possess powerful affinities for precisely those elements which are most prominently brought before the notice of chemists—such as the alkali elements, the halogens O, S, &c.—whereas nitrogen has the misfortune to possess but feeble affinities for such elements, but powerful affinities for such elements as Ti, Ba, B, Si, P, &c.

It should be remembered that O itself has but a feeble affinity for N, F, Cl, Br, I, &c.; and were these the only elements known, we would consider O to be quite as inactive an element as N appears to us under ordinary circumstances.

The compounds of O with Cl, for example, are characterised by their powerful explosive properties, just as are so many nitrogen compounds.

4. The affinity surface for hydrogen shows that it belongs to the alkali metal group, and not to the chlorine group of elements.
5. The point of maximum affinity shifts from F to Li as we pass from Li to F.

If we arrange in order the affinity surfaces of the elements of the first series of the Periodic System (viz., Li, Be, B, C, N, O, F) a remarkable fact becomes apparent. The affinity surfaces of the successive elements assume the appearance of successive positions of an advancing wave, whose crest, appearing on the extreme right-hand side of the diagram in the case of Li, sweeps from right to left as we pass from Li towards F, until at F the crest is on the extreme left-hand side. For example, in the case of Li the point of maximum affinity (*i.e.*, the highest point or crest of its affinity surface) is over F or Cl. Passing from Li to B the point of maximum affinity shifts towards N, BN being a body of very great stability. With C it lies over C itself, and hence the remarkable power of self-combination which C possesses. Its great involatility and its extraordinary hardness (diamond) are all evidences of the great attractive force with which C atoms cohere together.

Passing from C to N the point of maximum affinity shifts from C to B, BN being the more stable nitride N produces.

Passing from N to O, the point of maximum affinity shifts from B to Be or Li; finally passing from O to F, the point of maximum affinity shifts to Li, LiF being the most stable fluoride which F produces in this series.

The Periodic Law.

The Periodic Law shows that there is a connection between the atomic weights of elements and their properties, the connection being of such a nature that as the atomic weight increases the properties gradually alter, and then suddenly (after passing through an element of zero affinity, such as He or argon), at the end of a cycle, returns to nearly but not quite their original values. So that if the elements are arranged in the order of their atomic weights

—from H, the lightest, as unity to uranium, the heaviest, as 240—the series does not exhibit one continuous progressive modification in the physical and chemical characteristics of its several terms, but breaks up into a number of sections, in each of which the several terms present analogies with corresponding terms of the other series. Thus the whole series does not run*—

a, b, c, d, e, f, g, h, i, j, k, &c.,

but—

a, b, c, d, A, B, C, D, a, β , γ , δ , &c.

Now, the theory previously developed shows that the chemical properties of elements depend upon their attractive forces. Hence, if this theory is correct, there must be a connection between the atomic weights of elements and their attractive forces, the connection being of such a nature that as the atomic weight gradually increases the attractive forces gradually alter, and then suddenly return to nearly, but not quite, their original values—going through, as it were, cycles.

It is clear, therefore, that there must be a connection between the shape of the affinity surfaces of elements and their atomic weights, the shape gradually altering as the atomic weight alters, and then returning suddenly, at the end of a cycle, to nearly but not quite its original shape.

And this is actually the case. We find that if we arrange the elements in the order of their atomic weights, the affinity surfaces of the successive elements assume the appearance of successive positions of an advancing wave surface, whose crest, coming into the field of view on the extreme right-hand side of the diagram, gradually sweeps from right to left, altering its form continually as it passes down the field, then passes out of view on the left.

This is followed by the appearance of a new wave crest on the extreme right-hand side of the diagram, of nearly but not quite the original form, which then in its turn sweeps down the field of view and disappears, and so on; the one crest following the other like the successive waves on the sea-shore—the appearance of each new crest heralding the appearance of a new cycle of elements.

At the moment when the one crest passes out of the field of view on the left, and the second has not made its appearance on the right, we get an element of zero affinity belonging to the argon family.

As regards the elements of the odd series this is always the case. In the case of the elements of the even series this is not the case, for before the one wave crest has passed out of view, another crest has already begun to sweep down the field, and hence elements of zero affinity do not occur at all, but elements of intermediate properties such as Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt.

The complete memoir, with 40 plates of the affinity surfaces of 40 different elements, is now ready, and I hope to publish it in the course of this year. I am led to publish this preliminary note for various reasons, the chief among which is the fear that now my memoir has passed through several hands, I might be forestalled in the publication of these results.

University of Kiel.

REPORT OF THE COMMITTEE APPOINTED TO CONSIDER THE STANDARDISATION OF METHODS FOR THE BACTERIOSCOPIC EXAMINATION OF WATER.†

At the Congress of the Royal Institute of Public Health, held in the University of Liverpool, in July, 1903, a resolution was carried, on the motion of G. Leslie Eastes, Esq., M.B., B.Sc., that it was desirable that a committee should be appointed to consider the methods employed in the

bacterioscopic analysis of water, and, if possible, to draw up a scheme of uniform procedure for adoption in such examination, and to report to the next Congress of the Institute.

The Council of the Royal Institute of Public Health, in accordance with this resolution, appointed a committee of the following gentlemen:—

Professor Rupert Boyce, M.B., F.R.S. (chairman); the President of the Royal Institute of Public Health, Professor William R. Smith, M.D., D.Sc., F.R.S. Ed.; George M. Duncan, Esq., M.D.; G. Leslie Eastes, Esq., M.B., B.Sc.; John Eyre, Esq., M.D.; Major W. H. Horrocks, R.A.M.C., M.B., B.Sc.; William G. Savage, Esq., M.D., B.Sc.; Professor G. J. McWeeney, M.D.; Professor G. Sims Woodhead, M.D., F.R.S. Ed.; and Professor R. Tanner Hewlett, M.D., D.P.H. (Honorary Secretary).

REPORT OF THE COMMITTEE.

All the members of the Committee are in agreement that the minimal number of procedure should be:—

a. Enumeration of the bacteria present on a medium incubated at room temperature (18–22° C.).

b. Search for *Bacillus coli*, and identification and enumeration of this organism if present.

The committee regard these procedures as an irreducible minimum in the bacterioscopic analysis of water. The majority of the Committee recommend in addition:—

c. Enumeration of the bacteria present on a medium incubated at blood heat (36–38° C.).

d. Search for and enumeration of streptococci.

The Committee do not think it necessary as a routine measure to search for the *Bacillus enteritidis sporogenes*, but are agreed that in special or exceptional instances it may be advisable to look for this organism.

The Collection of the Sample.

No special precautions beyond those generally recognised are suggested for taking the sample. The samples should be collected in sterile stoppered glass bottles having a minimal capacity of 60 c.c. In special instances it may be desirable to have much larger quantities.

Unless examined within three hours of collection the sample must be ice-packed.

(The Committee recognise that under all circumstances the sooner the water is examined after collection the more reliable are the results obtained.)

Media to be Employed for Enumeration.

The choice of medium lies between distilled water gelatin, nutrient gelatin, distilled water agar, gelatin agar, and nutrient agar. The reaction of the medium is of importance.

For enumeration at room temperature any of these media may be employed, but for enumeration at blood heat an agar or gelatin agar must be used.

The Americans seem to be using an agar medium only, and although on the ground of simplicity it might be desirable to use a single medium for enumeration under all circumstances—e.g., a distilled water agar—it is felt by the Committee that gelatin media frequently give indications of value that are lacking with agar—viz., liquefaction of the medium by many organisms and the more characteristic appearance of the colonies in it; gelatin is therefore recommended.

Since with a polluted water (detection of pollution being the ultimate aim in water examination) nutrient gelatin gives a relatively larger number of colonies than distilled water gelatin, nutrient gelatin should be used when one gelatin only is employed. At the same time, it is recognised that cultures in distilled water gelatin compared with cultures in nutrient gelatin often give useful indications. Thus with an unpolluted water the number of colonies is usually relatively larger in distilled water gelatin than in nutrient gelatin; with a polluted water the converse is the case. Therefore the use of both gelatins (distilled

* The illustration is from Huxley, "Method and Results," pp. 76–77.
† From the *Journal of State Medicine*, August, 1904.

water and nutrient is desirable), sets of plates being made with each medium.

Similarly, it was felt by many members of the Committee that a comparison of the ratio of the number of organisms developing at room temperature to those developing at blood heat gives useful indications. With a pure water this ratio is generally considerably higher than 10 to 1, with a polluted water this ratio is approached, and frequently becomes 10 to 2, 10 to 3, or even less. The actual number of organisms growing at blood heat is also of considerable value apart from any question of ratio. Therefore it is suggested that plates of nutrient agar should also be employed and incubated at blood heat.

In certain instances it is true that this ratio may be unreliable. Thus with surface waters, especially in tropical countries (as pointed out by Major Horrocks) varieties of the *Bacillus fluorescens liquefaciens* and non *liquefaciens* and *Bacillus liquefaciens* may be abundant and grow well at blood heat.

Preparation and Reaction of Media for Enumeration.

a. *Distilled Water Gelatin*.—Ten per cent gelatin in distilled water, and brought to a reaction of + 10 (Eyre's scale).

b. *Nutrient Gelatin*.—Ten per cent nutrient gelatin, preferably made with meat (beef) infusion and Witte's peptone, and brought to a reaction of + 10 (Eyre's scale).

In hot weather it may be necessary to increase the percentage of gelatin.

Some members of the Committee advocate the use of meat extracts in place of meat infusion, on the score of convenience and uniformity of composition, Brand's Essence or Bovril's Essence of Meat being recommended as the best. It is the general opinion, however, that Liebig's Extract is less suitable for this purpose.

c. For enumeration of blood heat it is recommended that *nutrient agar* should be employed, being prepared with the same constituents as nutrient gelatin, but substituting 1½ per cent of powdered agar for the gelatin. Reaction + 10.

d. *Distilled Water Agar*.—Powdered agar 1½ per cent dissolved in distilled water, and brought to a reaction of + 10.

Owing to the changes which occur in the reaction of the medium on keeping, the media employed should preferably be not more than three weeks old.

Amounts to be Plated, Size of Dishes, &c.

Gelatin.—For an ordinary water amounts of 0.2, 0.3, and 0.5 c.c. may be plated in Petri dishes of not less than 10 c.m. diameter, preferably done in duplicate.

Agar.—Two plates may be made with 0.1 and 1.0 c.c., and are preferably duplicated.

In dealing with an unknown water, and in all cases of doubt, additional sets of plates should be prepared with a dilution of the water (made with sterilised tap-water) of ten or hundred fold, according to circumstances.

The amount of the medium in a plate should be 10 c.c.

The sample must be thoroughly shaken and mixed in all cases before plating.

Temperature of Incubation.

- | | | |
|---------------------|-------|-----------|
| a. Room temperature | | 18—22° C. |
| b. Blood heat | | 36—38° C. |

Counting.

Counting to be done with the naked eye, preferably in daylight, any doubtful colony being determined with the aid of a lens or low-power objective.

Time of Counting.—Gelatin plates should be counted at the end of seventy-two hours; but in all cases the plates should be inspected daily, in order that the count may be made earlier should liquefaction render this necessary.

The blood heat agar plates should be counted at the end of forty to forty-eight hours.

Search for *Bacillus Coli*.

Method.—The Committee recommend either—

a. The glucose formate broth method of Pakes.

b. The bile salt broth method of McConkey.

Incubation anaerobically at 42° C. increases the chances of success with either medium, and is strongly recommended.

It has also been suggested that the neutral-red (Grübler's) glucose broth medium may be employed.

The Committee do not regard with favour the Parietti method, or the use of carbohic acid media.

Quantity of Water to be Examined.

As a routine 50 c.c. should be the minimal quantity examined for the presence of the *Bacillus coli*, quantities from a minimum of 0.1 c.c. to a maximum of 25 c.c. being added to the tubes of culture media.

The Committee are of opinion that it is preferable to add the water directly to the tubes of culture medium, even with the larger amounts, rather than first to concentrate by filtration through a porcelain filter (the filter brushing method). The culture media recommended may be diluted with at least an equal volume of the water without interfering with their cultural properties, and large tubes or small flasks may be used for the larger amounts.

In the case of the bile salt lactose peptone water, the medium may for the larger amounts be prepared of double strength.

Isolation of *Bacillus Coli*, if present.

If indications of the presence of *Bacillus coli* be obtained in the preliminary cultivations, the organism must be isolated and identified.

This may be done by making *surface cultures* on plates of either—

- Litmus lactose agar, reaction + 10;
- Bile salt agar;
- Nutrose agar of Conradi and Drigalski; or
- Ordinary nutrient gelatin.

The best medium of all is, probably, the nutrose agar of Conradi and Drigalski. Agar media have the advantage of saving time.

Identification of, and Tests for, the *Bacillus Coli*.

Having obtained coli-like colonies on the plates made from the preliminary cultivations of the water, sub-cultures must be made in order to identify the organism. The following, at least, should be made:—

- Surface agar at 37° C. The abundant growth so obtained enables many sub-cultures and preparations to be made if required.
- Stab and surface cultures in gelatin. This may be done in the same tube.
- Litmus milk incubated at 37° C.
- Glucose litmus medium.
- Lactose litmus medium.
- Peptone water for indol reaction.

Characters of the *Bacillus Coli*.

The *Bacillus coli* is a small motile, non-sporing bacillus, growing at 37° C. as well as at room temperature. The motility is well observed in a young culture in a fluid glucose medium. It is decolourised by Gram's method of staining. It never liquefies gelatin, and the gelatin cultures should be kept for at least ten days in order to exclude a liquefying bacillus. It forms smooth, thin surface growths and colonies on gelatin, not corrugated, growing well to the bottom of the stab (facultative anaerobe).

It produces permanent acidity in milk, which is curdled within seven days at 37° C. It ferments glucose and lactose, with the production both of acid and of gas.

The typical *Bacillus coli* must conform to the above description and tests.

It generally also forms indol (best obtained in peptone water cultures), gives a thick yellowish-brown growth on

potato (greatly dependent on the character of the potato, sometimes (about 50 per cent) ferments saccharose, changes neutral red (Grübler's), and reduces nitrates, and half the gas produced by it from glucose is absorbable by KOH; and these tests, if time and opportunity permit, may be performed in addition to the foregoing.

The Committee recognise that atypical *Bacilli coli* are met with, but in the present state of our knowledge hesitate to make any suggestion with regard to their significance.

Streptococci.

The Committee consider that it is a distinct advantage to search for streptococci. They may be looked for by making hanging-drop preparations of the fluid media employed for the preliminary cultivation of the *Bacillus coli* (glucose formate broth, &c.). The presence or absence of streptococci in these tubes gives also a quantitative value to the examination, just as in the case of *Bacillus coli*, and the result obtained should be stated. The streptococci should be isolated (best carried out on nutrose agar plates), and their characters determined.

Bacillus Enteritidis Sporogenes.

As already stated, the Committee do not consider that it is essential as a routine procedure to search for the *Bacillus enteritidis sporogenes*, though in certain instances it may be of advantage to do so. A negative result in such cases is probably of more value than a positive one.

This report is the outcome of prolonged deliberations, and every point has been carefully considered and discussed by the members of the Committee.

In conclusion, the Committee suggest that if the above recommendations were to be adopted by all engaged in the bacteriological examination of water it would conduce to uniformity of results, and would render comparable the data obtained by different observers. An addendum might be added to a report on an analysis conducted on these lines, to the effect that the analysis had been carried out in conformity with the procedures recommended by the Committee of the Royal Institute of Public Health, 1904.

The Committee beg to acknowledge their great indebtedness to Prof. R. Tanner Hewlett, M.D., D.P.H., upon whom the great burden of the work of the Committee has devolved.

EFFECT OF MERCERISING ON DYE AFFINITY.

By W. P. DREAPER, F.I.C., F.C.S.

FOLLOWING my remarks on colloids and the action of dyes in my paper on "Gravity and Chemical Action" (CHEMICAL NEWS, vol. xc., p. 53), it would seem reasonable to assume that the additional affinity of mercerised cotton for dye-stuffs is due to the higher colloidal state of the fibre substance.

This action has been noticed by several observers, including Schaposchnikoff and Minajeff (*Zeit. f. Farb. und Text. Chem.*, 1903, No. 13; 1904, p. 163), Hübner and Pope (*Journ. Soc. Chem. Industry*, 1904, p. 404).

If this explanation is correct, it would follow that the ratio of colour taken up by the treated cotton and the natural fibre would be a constant one for ordinary dyes, assuming that the dyeing action is due to the higher colloid holding back a greater proportion of the dye, and that there is no additional chemical or other action between the fibre and the dye. The figures given by Schaposchnikoff and Minajeff in their articles indicate that in the majority of cases this is so. Working with such widely different substances as indigo, Diamine Blue 3 B (direct dye), and tannic acid, the ratio in each case is as 100 is to 140.

Although the authors do not seem to realise the importance of their figures, yet these figures are very in-

teresting from this point of view. For these figures indicate, so far as they go, the mechanical nature of the dyeing action in the above cases. The authors also examined the action of mercerised cotton on mordants in the same way. Here they do not indicate that the same ratio, 100—140, is obtained, but E. Knecht (*Journ. Soc. Dyers and Colourists*, 1903, p. 181) points out that their methods of estimating the results obtained are seriously at fault in this case. The absorption in this case may also be modified by the condition of the solution, &c.

The fact noted that a greater proportion of dye is required to produce the same shade in the case of the mercerised fibre is probably to be explained on physical or optical grounds, and has little to do with the direct action of the dyes as expressed by their absorption values.

The further values promised by the authors on insoluble azo-dyes, sulphide colours, and even aniline black, although necessarily of a more complicated order, should be of great interest.

This relative action of dyes on fibre material may in time afford a direct measurement of the colloidal state of the fibres in terms of their relative absorption.

From this point of view the difference between the dyeing properties of direct and ordinary dyes on cotton would be a measure of their relative colloidal properties. Mosenthal (*Journ. Soc. Chem. Industry*, vol. xliii., p. 292) has pointed out the extremely porous nature of the cuticle of the cotton fibre. It had previously been assumed that the dyeing action of the cotton fibre (Crum, *Journ. Chem. Soc.*, vol. i., p. 409) was due to capillary action, the cuticle being non-porous. Still, arguing from the above point of view, the "mesh" of the cotton fibre would be too large to hold the ordinary acid dyes, but able to hold or retain the tetrazo or higher colloid dyes. It may be pointed out in confirmation of this view that artificially prepared filaments of cellulose (artificial silk), which without much alteration in chemical composition are in a highly colloidal state, easily retain ordinary acid colours.

It is of course possible that when once a dye is retained by this colloid action that solid solution, or even condensation, may play some part in the action.

When Cross and Bevan (*Journ. Soc. Chem. Industry*, vol. xiii., p. 354) criticised Dr. Weber's theoretical conclusions on the ground that he assumed a one-sided penetrability, they overlooked the possibility of some such retaining action on the part of the fibre. This would produce the dyeing action.

Perhaps the difference between the fastness of ingrain dyes when dyed direct to those "developed" or dyed ingrain (Dreaper, *Journ. Soc. Chem. Industry*, vol. xiii., p. 95) may be due to the fact that in direct dyeing we only get this colloid precipitating action. In the case where the dye is actually developed or produced in the fibre itself, we may be working under such conditions that actual or at least a more perfect solid solution obtains. This would agree with the fact I brought forward, that the dyes are still fast against boiling out after the phenolic dyed samples are treated with dilute caustic alkali, in which solution the dye is very soluble. The alternative idea put forward by Prof. Green in the discussion following my paper (*Ibid.*), that the ingrain dyed sample was fast because of the increased size of the aggregates formed in the fibre space, does not explain why the dye is still fast after the above treatment. If, in place of this action, we had solid solution, the action of the alkali would probably be as non-effective as it is in practice. The idea is therefore put forward that the increased affinity of mercerised cotton for dye-stuffs is a measure of the increased colloidity of the fibre.

In conclusion I would put forward a plea for greater accuracy of detail in the experiments carried out in connection with the theory of dyeing. The discussion carried on at the present time seems to turn almost entirely on the mistakes of individual experimenters. Until experiments are conducted on closer and more careful lines we shall remain in the present state of uncertainty.

THE PRODUCTIONS OF MAGNETIC ALLOYS
FROM NON-MAGNETIC METALS.*

By R. A. HADFIELD.

It is thought that the following description of the Heusler alloys may be of interest to the Section.

Having some years ago produced a non-magnetic iron alloy, known as "manganese steel," I was much interested in learning from Dr. Heusler that, with the same metal (manganese) which had enabled me to obtain a practically non-magnetic iron alloy, it had been found possible to produce a magnetic copper alloy.

I have had communications with Dr. F. Heusler, who has given me much interesting information regarding these special alloys, and have myself also produced some of them.

It is, of course, well known that the metals copper, aluminium, and manganese are non-magnetic. It is therefore, to say the least, surprising to find that, combined in certain proportions, they produce an alloy having quite considerable magnetic properties.

It may be first mentioned that no combination of copper with aluminium produces a magnetic alloy; the peculiar change noticed, therefore, must be ascribed entirely to the presence of the metal manganese—the same metal which, in manganese steel, produces the profound change in iron, converting it from its well-known magnetic to non-magnetic condition.

As it was thought that perhaps the metal manganese under certain conditions might show some reversibility, as is the case with certain iron-nickel alloys, which, whilst being non-magnetic at ordinary temperatures, become magnetic at low temperatures, -60° to -80° C., Sir James Dewar himself submitted to the temperature of liquid air the manganese metal I used in producing the alloy exhibited. No change was found to occur; the metal remained as non-magnetic as at ordinary temperatures. This, of course, under the same test was found to be the case with the copper and aluminium used in my experiments.

The alloy exhibited contained 60 per cent copper, 25 to 27 per cent manganese, and 12 per cent of aluminium. The manganese metal used contained about 92 per cent of manganese, the rest being 6 to 7 per cent of silicon, 0.5 to 1 per cent of carbon, and probably 0.50 per cent of iron. But Dr. Heusler has shown that with absolutely no iron present the magnetic qualities are exactly the same.

Another very curious point is that, whilst it must be the manganese which confers the magnetic properties, the "reversibility," so to speak, is brought about by the aluminium.

For example, with the manganese fairly constant (25 to 28 per cent) and the aluminium varying from 3 to 14 per cent, the magnetisability with 3 per cent is nil, 5 per cent confers a little, 10 per cent is still more, the maximum being reached with 14 per cent aluminium.

Specimen number.	Analysis (per cent).		H = (magnetising force).			
	Mn.	Al.	20.	40.	100.	150.
34.	28	3.6	Nonmagnetisable.			
35.	28	5.7	Very slightly magnetisable.			
36.	26	9.6	2220	2670	3200	3470
32.	26	14.6	4500	4850	5380	5550
33.	25	13.8	3580	4075	4645	4900

B =

From the above list it will be seen that Dr. Heusler finds the magnetisability of the alloy will increase with an increased percentage of aluminium, the maximum for any stated percentage of the manganese being attained when the aluminium percentage amounts to (roughly) one-half of the percentage of manganese; or, in other words, when the alloy contains one atom of aluminium to one atom of manganese.

It may be added that the alloy exhibited is unfortunately very brittle, and all attempts to forge it cold or hot at various temperatures, even only at dull red, have been unsuccessful.

It may be further added that the alloy is faintly magnetic immediately after casting, but becomes non-magnetic when heated to about 170° and quenched in cold water.

But by continued heating to about 80 – 150° magnetisability reappears and in an intensified degree. The unstable magnetic condition becomes stable.

Other metals may be introduced without causing the alloy to lose its magnetic properties.

For example, lead may be introduced. The alloy is then more fusible, the transformation-point is lowered, and, under suitable heat treatment conditions, the magnetisability is even increased. Tin is another example; 10 per cent gives magnetisability, the maximum being obtained with 21 to 22 per cent of tin to 30 per cent of manganese.

Alloys of antimony and manganese, no copper being present, are also magnetic.

THE ACTION OF CERTAIN GASES ON
GLASS IN THE NEIGHBOURHOOD OF HEATED
METALS.*

By G. T. BEILBY.

In a former paper (*British Association Report*, Southport, 1903) I described the formation of halos around pieces of metal-foil on glass plates when these are heated to a sufficient temperature in the presence of the products of combustion of coal-gas and air. The form of the halos themselves, as well as the formation of corresponding images of the metal on glass plates placed at a little distance above the heated metal, suggested that the effects were produced either directly or indirectly by particles thrown off from the hot metal. The halos and images were found to consist of the decomposition products of the glass itself, silica and soluble alkaline salts, and the chemical agent in the decomposition was seen to be one or other of the gases of the surrounding atmosphere. Two matters for further inquiry therefore presented themselves:—(1) To what chemical agent is the decomposition of the glass due? And (2) what is the cause of the localisation of this decomposition in the immediate neighbourhood of the hot metal as shown in the formation of halos or images?

The first of these questions was settled by a series of experiments in which glass slips with small pieces of platinum-foil laid upon them were heated in a glass tube through which specially prepared gases were led. The tube, of course, served to completely exclude the products of combustion given out by the heating burner. The glass slips were heated to 500 – 600° , while a current of gas was passed through the tube at the rate of a litre per hour. After heating for an hour the glass slips were allowed to cool down slowly to the atmospheric temperature, and were then examined and compared with each other, and with similar slips which had been heated on a hot plate with free access of the products of combustion of coal-gas and air.

Experiment 1.—With air which had been freed from CO_2 and other acid gases, and then dried by passing it over CaCl_2 . No halo was visible on the slip till it was breathed on, when a very faint but distinct halo appeared.

Experiment 2.—With air which had been freed from CO_2 and then saturated with water vapour by bubbling it through water at 50° . A distinct halo was produced, but the decomposition of the glass had been very much less energetic than it would have been in the presence of combustion products. From the marked effect produced by the addition of water vapour it seems probable that if the air in Experiment 1 had been more perfectly dried, not even the faint halo would have been produced.

* Read before the British Association (Section A), Cambridge Meeting, 1904.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

Experiment 3.—With CO_2 dried to the same extent as the air in Experiment 1. No halo was visible till the slip was breathed on, when an even fainter halo than that observed in Experiment 1 appeared.

Experiment 4.—With air which had been shaken up with a saturated aqueous solution of SO_2 , and afterwards dried as in Experiment 1. A well-defined halo appeared, comparable in distinctness with those produced in the presence of the products of combustion.

When these halos are breathed on so that a film of moisture condenses momentarily on the surface of the glass and then evaporates, the salts which have been dissolved by the water re-crystallise and become markedly separated from the insoluble films of silica. The microscopic appearance of this crystallisation correspond with that of sodium sulphate, and the solution of these salts gives a precipitate of barium sulphate. It may therefore be concluded that the decomposition of the glass is due to the action of sulphuric anhydride which has been formed by the union of SO_2 with O.

Experiment 5.—The same mixture of air and SO_2 was bubbled through an aqueous solution of SO_2 maintained at 50° , thus raising the proportion of SO_2 and H_2O in the gas.

The entire surface of the glass slip, as well as that of the heated part of the interior of the glass tube, was now covered with a white film of decomposed glass, the spot on which the platinum-foil had lain being marked out by its being less thickly covered with the white film. In this case it was evident that the increased proportions of SO_2 and H_2O in the gas had enabled the combination to take place with such freedom that the accelerating action of the hot metal was now relatively small.

Experiment 6.—A portion near the centre of a glass tube was heated to about 600° . A fine glass tube containing a little sulphuric acid was placed in the tube sufficiently near the heated part to volatilise the sulphuric acid slowly. A slow current of air was passed through the heated tube in the direction which enabled it to carry the SO_3 and H_2O evolved by the acid through the heated portion.

In a few minutes the interior surface of the heated portion of the tube was covered with a white film of decomposed glass to all appearance identical with the films developed in Experiment 5.

This experiment further confirms the conclusion that the attack on the heated glass is made by SO_3 .

The familiar phenomenon of the formation of a dull white film on the surface of glass vessels, which have been heated above a certain temperature in gas furnaces or muffles, evidently results from this action of SO_3 on the silicates of the glass. When the action has been slight the entire film may be washed off, leaving a perfectly polished surface, but after long continued or severe action the surface of the glass is permanently roughened. This appearance is often mistaken for devitrification of the glass, but microscopic examination shows that the roughened surface is not crystalline, but finely granular, and very similar to that produced by the action of a mixture of gaseous hydrofluoric acid and air.

Experiments 1 and 2 show that moist air also attacks and decomposes glass, but this action is so slight that it has only been observed in the immediate neighbourhood of the hot platinum.

The second question proposed at the outset of this paper was:—What is the cause of the localisation of the decomposition of the glass in the immediate neighbourhood of the hot metal as shown by the formation of halos or images? The preceding observations having shown that the active chemical agent in the production of these appearances is sulphur trioxide, the suggestion naturally occurs that it is the presence of the hot metal which determines the formation of SO_3 by the union of SO_2 with O. The influence of solid catalysts in bringing about this synthesis is well known, and the subject might therefore have been dismissed without further experiment or discussion had it not been that the opportunity appeared to be a favourable one for obtaining information as to whether the action takes place

wholly on the surface of the hot metal, or whether it also occurs in the atmosphere surrounding the metal.

If the SO_3 molecules are formed on the surface of the metal, they ought at once to diffuse into the surrounding atmosphere, being quickly separated from their fellow molecules among the vastly preponderating number of molecules of the other gases composing that atmosphere.

Taking the coal-gas used as of average purity as regards sulphur, the proportion of SO_3 present in the atmosphere could not exceed 1/50,000. But when the forms and disposition of the halos and images around and above the metal are studied, it is seen that they do not correspond very satisfactorily with the above views as to the immediate diffusion of the SO_3 molecules in the surrounding atmosphere. The halos and images are to some extent permanent records of the course followed by these molecules, and as such they distinctly suggest that the molecules of SO_3 have travelled together from the metal surface, and that they have remained in company to a much greater extent than might have been expected had their movements been simply determined by molecular diffusion. The appearances rather suggest that the agent which caused them was in the form of a cloud of projectiles, some of which were carried up to the under surface of the covering glass which they attacked, producing the image, while the greater number, falling short of this, fell back on the surface of the lower glass slip, producing the halo around the metal.

The disintegration of hot platinum has been recently studied by Holborn and Austin (*Phil. Mag.*, April, 1904, p. 388), who have found that at temperatures above 1150° the loss of weight from a platinum surface of 150 sq. m.m. in thirty minutes was quite weighable. But from the rate of decrease of this loss with falling temperature, it is evident that at the temperatures used in my experiments, 500 – 600° , the loss over this short period would be quite unweighable. Nevertheless, taking these observations in connection with those of Richardson (*Phil. Mag.*, July, 1903, p. 80) on the "Positive Ionisation produced by Hot Platinum in Air at Various Pressures," it appears not improbable that there is an actual if slow disintegration at the lower temperature, in which case the particles or ions thrown off might play the double part of projectiles and nuclei.

Experiments have been made on sweeping the nuclei forward from the hot platinum with pure air and with pure nitrogen; these gases being afterwards allowed to intermingle with the products of combustion in contact with a hot glass surface. In neither case was the action on the glass sufficiently distinct to enable it to be definitely attributed to the nuclei carried over from the platinum. The products of combustion themselves appear to carry with them sufficient nuclei to determine the formation of SO_3 in sufficient quantity to produce a slight general attack all over the heated glass surface. This attack effectually masks the slighter effects which result from any nuclei which may be carried over from the platinum in the above experiment.

It cannot be claimed for these observations that they give a conclusive answer to the question, "What is the cause of the localisation of the decomposition in the neighbourhood of the hot metal?" but they certainly do not give a final negative to the suggestion that some part of this effect is due to ionisation produced by the hot metal.

Synthesis of Estragol and the Aromatic Derivatives with Non-saturated Chain.—M. Tiffeneau.—The synthesis of estragol, which the author realised by means of the magnesium derivatives, has since been published by other chemists. His results, however, show that allyl iodide and bromide react on the organo-magnesium compounds, even in the cold, whilst the other non-saturated halogen derivatives only unite after almost complete elimination of the ether, and at a temperature of 100° or more.—*Comptes Rendus*, cxxxix., No. 10.

A REACTION FOR KETO-HEXOSES.*

By HENRY J. HORSTMAN FENTON, F.R.S.

By oxidation of lævulose, cane-sugar, inulin, or sorbose in presence of ferrous iron at about 90–100°, and heating the resulting solution with phenylhydrazine-*p*-sulphonic acid, a compound is obtained which dyes silk a rich brownish pink colour, which is remarkably stable and permanent. This reaction appears to be especially characteristic of keto-hexoses or substances which yield them on hydrolysis, and is given by dextrose, milk-sugar, maltose, or starch only to a limited extent or not at all.

A COLOUR REACTION FOR METHYLFURFURAL AND ITS DERIVATIVES.*

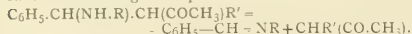
By H. J. H. FENTON, F.R.S., and J. P. MILLINGTON, B.A.

WHEN bromomethyl-furfural is heated with dimethylaniline and a dehydrating agent, such as phosphorus oxychloride, zinc chloride, or dry oxalic acid, an intensely blue-coloured compound is obtained. This reaction is extremely sensitive, and is given by bromo-, chloro-, iodo-, or acetoxy-methylfurfural, and by methylfurfural itself, but not by the condensation products previously described (Fenton and Gostling, *Trans. Chem. Soc.*, 1899, 423; 1901, 807). As a dye the blue colour appears to be very permanent in the dark, but slowly fades in sunlight.

THE ACTION OF ORGANIC BASES ON OLEFINIC KETONIC COMPOUNDS.*

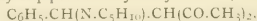
By S. RUHEMANN and E. R. WATSON.

THE authors have continued their investigations of the behaviour of unsaturated ketonic compounds (*cf. Trans. Chem. Soc.*, 1904, lxxv., 466), especially of benzylidene-acetylacetone, towards organic bases, and have isolated several additive compounds which are thus formed, *e.g.*, with *m*-toluidine, *p*-toluidine, *m*-chloroaniline, *p*-chloroaniline, *β*-naphthylamine. These compounds, on heating, suffer the following decomposition:—



In some cases the additive compounds cannot be isolated, since they are decomposed at once according to the above equation. Of interest is the fact that neither *o*-toluidine nor *α*-naphthylamine combine additively with benzylidene-acetylacetone. *o*-Substituted benzenoid bases, therefore, seem not to react with the diketone. This conclusion is supported by the fact that piperidine readily forms an additive product with benzylideneacetylacetone, but tetrahydroquinoline does not.

The study of piperidobenzylacetylacetone,—



the additive compound formed from benzylideneacetylacetone and piperidine, has proved of the greatest interest as throwing light on the catalytic action of piperidine and other secondary bases in the condensations of aldehydes and ketones which have been elaborated by Knoevenagel and his pupils.

Taking the formation of benzylidene-*bis*-acetylacetone as example, the authors arrive at the view that the reaction is to be expressed thus:—

1. $\text{C}_6\text{H}_5\cdot\text{CH}(\text{CO}\cdot\text{CO}\cdot\text{CH}_3)_2 + \text{C}_5\text{H}_{10}\cdot\text{NH} = \text{C}_6\text{H}_5\cdot\text{CH}(\text{N}\cdot\text{C}_5\text{H}_{10})\cdot\text{CH}(\text{CO}\cdot\text{CH}_3)_2.$
2. $\text{C}_6\text{H}_5\cdot\text{CH}(\text{N}\cdot\text{C}_5\text{H}_{10})\cdot\text{CH}(\text{CO}\cdot\text{CH}_3)_2 + \text{CH}_2(\text{CO}\cdot\text{CH}_3)_2 = \text{C}_6\text{H}_5\cdot\text{CH}(\text{CH}_2\text{CO}\cdot\text{CH}_3)_2 + 2\text{H}_2\text{O}.$

* Read before the British Association (Section B), Cambridge Meeting, 1904.

Also Knoevenagel and Faber's observation (*Ber.*, xxxi., 2773), that ethyl benzylideneacetoacetate in the presence of diethylamine yields ethyl benzylidene-*bis*-acetoacetate, has found a ready explanation. The fact that piperidobenzylacetylacetone, on treatment with water, yields benzaldehyde and benzylidene-*bis*-acetylacetone indicates that the formation of the latter substance is preceded by the production of an additive compound of the unsaturated ketone with the bases.

THE DECOMPOSITION AND SYNTHESIS OF AMMONIA.*

By EDGAR PHILIP PERMAN.

It is well known that on heating ammonia a large proportion of it is decomposed, and it has been assumed by many chemists that the mixture then comes into chemical equilibrium: some experiments recently carried out by Mr. G. A. S. Atkinson and myself seem to disprove the existence of any equilibrium in the case.

Decomposition of Ammonia by Heat.—In a recent paper (*Proc. Roy. Soc.*, lxxiv., 110) it was shown, from observations on the rate of decomposition of ammonia heated in a porcelain globe, that there is no equilibrium until complete (or nearly complete) decomposition has taken place, and that the reaction is mono-molecular.

Direct Synthesis of Ammonia by Heat.—To solve the question of equilibrium, it was thought better to attempt to reach the equilibrium point, if any, by synthesis. A mixture of nitrogen and hydrogen (1:3) was passed slowly through a red-hot glass tube into dilute acid; the solution was then made alkaline, and tested for ammonia by Nessler's solution; *not a trace was found*. The result was similar when the tube was packed with broken porcelain. If, however, the mixture was passed over red-hot iron (or many other metals) or over asbestos, pumice, or clay tobacco-pipe stems, traces of ammonia were formed. These last-named substances contain iron, and it is concluded that there is no combination of the nitrogen and hydrogen unless there is some catalysing agent present.

Decomposition and Synthesis of Ammonia by Electricity.—Traces of ammonia were formed on sparking a mixture of nitrogen and hydrogen, and the gases came into equilibrium (with the apparatus used) in about thirty minutes. Approximately the same equilibrium point was reached on decomposing ammonia by sparking, but when the volume was kept constant many hours' sparking were required to reach that point.

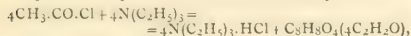
ON THE PRODUCTS OBTAINED BY THE ACTION OF TERTIARY BASES ON SOME ACID CHLORIDES.*

By Professor EDGAR WEDEKIND.

THE author has previously shown (*Annalen*, cccxviii., 99; cccxxiii., 257) that, in spite of the violent reaction which occurs between the chlorides of powerful acids and strong tertiary bases, no quaternary salt of the type $\text{R}_3\text{N}\cdot\text{CO}\cdot\text{Cl}$ is produced, but that the hydrochloride of the tertiary amine, $\text{R}_3\text{N}\cdot\text{H}\cdot\text{Cl}$, is obtained in quantitative yield. This fact is in so far of importance in connection with the stereochemistry of nitrogen, as it indicates the reluctance of the trivalent nitrogen atom to take up two acidic or negative groups; the trivalent nitrogen atom exhibits a kind of striving to assume the most stable condition—that, namely, of which ammonium chloride is the type.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

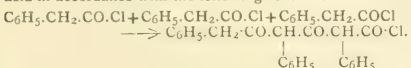
The question at once arises in connection with the above reaction as to what becomes of the residue of the acid chloride molecule; the solution of this problem presented extraordinary experimental difficulties, but its study has led to the discovery of several interesting facts which may here be briefly mentioned. The author has already shown that by the action of acetyl chloride on triethylamine, pyridine, &c., dehydracetic acid is produced (*Annalen*, cccxxiii., 247); in this reaction four molecules of each component take part in accordance with the equation—



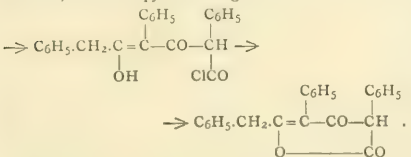
but when the acetic chloride is replaced by propionyl, phenylacetic, or hydrocinnamic chloride, products are obtained which have only three times the molecular weight of the hypothetical substance which must be supposed to be first formed by the splitting off of hydrogen chloride from the *one* molecule of the acid chloride. Thus, the condensation product from propionic chloride, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Cl}$, has the empirical formula $\text{C}_9\text{H}_{14}\text{O}_3$ or $3(\text{C}_3\text{H}_5\text{O})$, and that from phenylacetic chloride, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Cl}$, corresponds to the formula $\text{C}_{24}\text{H}_{18}\text{O}_3$ or $3(\text{C}_8\text{H}_6\text{O})$.

The latter substance proved to be fairly easily obtainable, and the first supposition that it might be a phloroglucinol derivative—the symmetrical triphenylphloroglucinol—was found untenable, because the material can under no conditions be reduced to triphenylbenzene, and is relatively very stable even in alkaline solutions. The new compound shows simultaneously the behaviour of a lactone, a monoketone, and a primary alcohol; thus it gives with soda a monosodio-derivative, with hydroxylamine a monoxime, with acetic chloride a monoacetyl compound, and with benzoyl chloride a monobenzoyl derivative. On treating it with ammonia under pressure it yields a very stable pyridine derivative, and this reaction shows it to be a simple homologue of pyronone. (The previously known pyronone compounds contain, like dehydracetic acid, a carboxyl group in the side chain).

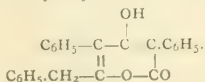
The mechanism of the reaction by which the substance is formed (compare J. N. Collie, *Trans. Chem. Soc.*, lxxvii., 971) would seem to be that three molecules of the acid chloride first condense with evolution of two molecules of hydrogen chloride, yielding the chloride of an α -diketonic acid in accordance with the following scheme:—



This hypothetical chloride then undergoes total or partial conversion into an enolic form, from which by subsequent loss of hydrogen chloride, in which the hydroxyl group is involved, the closed pyronone ring is formed—



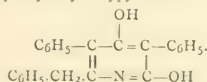
Since this pyronone derivative differs from those previously studied in that it gives an oxime as well as a monobenzoyl-derivative, it must be regarded as tautomeric in that it can assume the above ketonic form as well as the following enolic or hydroxylactonic constitution:—



The latter formula naturally gives rise to the acidic

derivatives. The remarkable power which the carbonyl group in the closed ring possesses of reacting with hydroxylamine must be attributed to the multiplication of unsaturated groups in the molecule, namely, to the presence of two phenyl groups and two double bonds in the closed chain.

As was to be expected from the known behaviour of pyrone or pyronone compounds, the action of ammonia gives benzylidiphenyldihydroxypyridine—



Lastly, it may be mentioned that the author has made a remarkable observation upon the interaction of isobutyric chloride with tertiary amines; in this reaction an extremely volatile substance crystallising in colourless needles and having an odour of menthol and camphor is obtained. This product is formed by the condensation of only two molecules of the acid chloride, and is not a pyronone derivative but a diketone; it is in all probability a tetramethylene derivative from which the author hopes to prepare the parent hydrocarbon.

SAPONARIN:

A GLUCOSIDE COLOURED BLUE BY IODINE.*

By G. BARGER.

THE substance known to botanists as "soluble starch," and occurring in the leaf epidermis of a number of plants, has been isolated from *Saponaria officinalis* at the suggestion of Professor L. Errera, of Brussels; it is a glucoside, and has been named *saponarin*. The substance is obtained pure in the shape of minute needles by a special method of crystallisation from mixtures of pyridine and water. Saponarin is insoluble in water and all ordinary organic solvents, but readily soluble in dilute alkalis and in pyridine; it melts at 231° with decomposition. The solution in alkalis is intensely yellow, and when acidified the substance remains for a long time in a state of pseudo-solution; in this condition it gives an intense blue or violet colouration with iodine dissolved in potassium iodide solution.

The air-dried crystals of saponarin lose water when heated or when left *in vacuo* over sulphuric acid. The dried substance is extremely hygroscopic, and, if left in the balance case for an hour or so, takes up quantitatively the water it had previously given off. For combustions it was dried *in vacuo* till of constant weight, and the boat containing it was then placed in a stoppered weighing tube. The mean of five analyses of the substance dried in this way gave—

C = 53.75 per cent, H = 5.16 per cent.

For the molecular weight determination pyridine was the only available solvent. The microscopic method was the most convenient, and gave the following result:—

A solution of 0.299 grm. in 2.96 grms. of pyridine was isotonic with a benzil solution of 0.23 mols. Hence M = 436.

The two possible formulae for saponarin are:—

$\text{C}_{19}\text{H}_{22}\text{O}_{11}$, requiring C 53.52, H 5.21, M 427

and—

$\text{C}_{21}\text{H}_{24}\text{O}_{12}$, requiring C 53.85, H 5.13, M = 468.

Of these the second is considered the more probable, but a definite choice cannot be made till the decomposition products of the substance have been studied more fully. On boiling saponarin with mineral acids it is hydrolysed,

* Read before the British Association (Section D), Cambridge Meeting, 1904.

and a yellow solution is formed, from which glucose was separated as phenyl glucosazaine. Unless the solution be dilute, a second product of hydrolysis separates as a thick yellow oil, which has not yet been obtained crystalline. The name *saponaretin* is suggested for it, and it is scarcely soluble in water, but dissolves in alkalis and in pyridine; it closely resembles the parent substance, but does not give the reaction with iodine. From dilute solutions saponaretin separates in the solid state, either amorphous or in the form of imperfect whetstone-shaped crystals. It has not yet been obtained quite pure, but seems to be mixed with another substance which crystallises from alcohol in glistening plates.

The formula of the latter substance has not been definitely fixed owing to want of material, but it seems to be a hydrate of saponaretin.

Saponaretin is in all probability closely allied to the flavones. When fused with potash it yields β -oxybenzoic acid, and a red solution which gives the phloroglucin reaction with pinewood. Phloroglucin itself could, however, not be isolated.

The blue substance formed from iodine and saponarin exhibits a close analogy with that formed from iodine and starch. Its composition varies considerably, and it is another example of the absorption of iodine by a substance in pseudo-solution. The blue substance has been obtained in the crystalline state, but must nevertheless be regarded as a mixture and not as a chemical compound.

LUTES.*

By SAMUEL S. SADTLER.

The subject of plastic cements used to secure joints in vessels and connections (generally for temporary purposes), has been rather neglected in the chemical literature.

The success or failure of processes has very seldom depended upon the choice of satisfactory lutes, but great annoyance has been experienced in chemical works and manufacturing places where only unsuitable compounds have been found to seal apertures in nitric acid, chlorine, hydrogen sulphide, and illuminating gas apparatus, and frequently considerable damage to property and loss of life has resulted.

I have therefore thought it advisable to bring together under the one title such formulae as I know to be reliable, or have reasonable grounds for believing so, and hope they may be useful to others for laboratory or works' use.

The majority of these cements are useful for purposes of preventing the escape of inert gases, and others are suitable for more or less special purposes, where corrosive gases, &c., come in contact with them. Many of them had to be put down from memory, and therefore the product obtained in their use may be a little too stiff or too thin, but such deficiencies could be easily regulated.

Lutes always consist of a menstruum and dissolved or suspended solids, and they must not be attacked by the gases and liquids coming in contact with them. In some cases the constituents of the lute react to form a more strongly adhering mass.

The conditions of application are, in brief:—

- a. Heating the composition to make it plastic until firmly fixed in place.
- b. Heating the surfaces.
- c. Applying the lute with water or a volatile solvent, which is allowed to volatilise.
- d. Moistening the surfaces with water, oil, &c. (the menstruum of the lute itself).
- e. Applying the lute in workable condition, and the setting taking place by chemical reactions.
- f. Setting by hydration.
- g. Setting by oxidation.

These principles will be found to cover nearly all cases. Joints should not be ill-fitting, depending upon the lute to do what the pipes or other parts of the apparatus should do. In most cases one part of the fitting should overlap the other, so as to make a small amount of the lute effective and to keep the parts of the apparatus rigid, as a luted joint is not supposed to be a particularly strong one, but rather one quickly applied, effective while in place, and easily removed.

Very moderate amounts of the lute should be used, as large amounts are likely to develop cracks, be rubbed off, &c.

A classification may be given as follows:—

- I. Plaster-of-Paris.
- II. Hydraulic cement.
- III. Clay.
- IV. Lime.
- V. Asphalt and pitch.
- VI. Resin.
- VII. Rubber.
- VIII. Linseed oil.
- IX. Casein and albumen.
- X. Silicates of soda and oxychloride cements.
- XI. Flour and starch.
- XII. Miscellaneous, including core compounds.

I. Plaster-of-Paris.

Plaster-of-Paris is, of course, often used alone as a paste, which quickly solidifies, for gas and wood distillation retorts, &c., and similar places where quickness of setting is requisite. It is more often, however, used with some fibrous material to give it greater strength. Asbestos is the most commonly used material of these, as it will stand a high temperature. When that is not so important, straw, plush trimmings, hair, &c., are used as binders, while broken stone, glass, and various mineral substances are used as fillers, but they do not add anything to the strength. These lutes seem to be particularly suitable for oil vapours and hydrocarbon gases.

Formulae:—1. Plaster and water.

2. " (wet) and asbestos.
3. " " " straw.
4. " " " plush trimmings.
5. " " " hair.
6. " " " broken stone, &c.

II. Hydraulic Cement.

Cement is used either alone or with sand, asbestos, &c., and I have been informed that these lutes are suitable for nitric acid. When used with substances such as resin or sulphur, it is probably employed because it is in such a fine state of division and used as a filler, and not because of any powers of setting by hydration.

Formulae:—1. Cement (neat).

2. " and asbestos.
3. " and sand.

III. Clay.

This most frequently enters into the composition of lutes as a filler, but even then the very finely-divided condition of certain grades renders it valuable, as it gives body to a liquid, such as linseed oil, which, unless stiffened, would be pervious to a gas, the clay in all cases being neutral. Thus, for luting pipes carrying chlorine, a stiff paste of clay and molasses has been suggested by Theo. Köller in *Die Surrogate*, but I cannot recommend it, as it soon gives way.

Formulae:—1. Clay and linseed oil.

2. Same, using fire-clay.
3. Clay and molasses.
1. Is suitable for steam, &c.,
2. For chlorine, and
3. For oil vapours,

* From the *Journal of the Franklin Institute*, clviii., No. 5.

IV. Lime.

Lime is used in the old lute known as putty, which consists of caustic lime and linseed oil. Frequently the lime is replaced by chalk and china-clay, but the lime should be, in part at least, caustic, so as to form a certain amount of lime soap. Lime is also used in silicate and casein compositions, which are very strong and useful, but will be described elsewhere.

Formula:—1. Lime and boiled oil to stiff mass.

2. Clay, &c., " "

V. Asphalt and Pitch.

These substances are used in lutes somewhat interchangeably. As a rule, pitch makes the stronger lutes. Tar is sometimes used, but, because of the light oils and (frequently) water contained, it is not as good as either of the others.

Asphalt dissolved in benzol is very useful for uniting glass for photographic, microscopical, and other uses. Also for coating wood, concrete, &c., where the melted asphalt would be too thick to cover well. Benzol is the cheapest solvent that is satisfactory for this purpose, as the only one that is cheaper would be a petroleum naphtha, and it does not dissolve all the constituents of the asphalt. For waterproofing wood, brick, concrete, &c., melted asphalt alone is much used, but when a little paraffin is added it improves its waterproofing qualities, and in particular cases boiled oil is also added to advantage.

Parts.

Formula:—1. Refined lake asphalt.

2. Asphalt	4
Paraffin	1
3. Asphalt	10
Paraffin	2
Boiled oil	1

Any of these may be thinned with hot benzol or toluol. Toluol is less volatile than benzol and about as cheap, if not cheaper, the straw-coloured grades being about 24 cents per gallon.

Examples of so-called "Stone Cement" are:—

	Parts.
4. Pitch	8
Resin	6
Wax	1
Plaster	$\frac{1}{2}$ to $\frac{1}{4}$
5. Pitch	8
Resin	7
Sulphur	2
Stone powder	1

These compositions are used to unite slate slabs and stoneware for domestic, engineering, and chemical purposes. Various resin and pitch mixtures are used for these purposes, and the proportions of these two ingredients are determined by the consistency desired. Sulphur and stone powder are added to prevent the formation of cracks; sulphur acting chemically and stone powder mechanically. Where the lute would come in contact with acid or vapours of the same, limestone should not be the powder used, otherwise it is about the best. Wax is a useful ingredient to keep the composition from getting brittle with age.

A class of lutes under this general grouping that are much used are so-called "Marine Glues." They must be tough and elastic. When used for caulking on a vessel they must expand and contract with the temperature, and not crack or come loose.

Parts.

Formula:—6. Pitch	3
Shellac	2
Pure crude rubber	1
7. Pitch	1
Shellac	1
Rubber substitute	1

These are used by melting over a burner.

(To be continued).

ROYAL TECHNICAL INSTITUTE, SALFORD.

Principal—H. B. KNOWLES, M.A.

SESSION NOW COMMENCING. Full DAY COURSES AND EVENING CLASSES in various subjects, including CHEMISTRY, DYEING, and CALICO-PRINTING. Special Evening Courses for "MANCHESTER TRADE"—ANALYSIS OF DYES, DYEWARES, &c., and GAS ANALYSIS. Dayhouse contains Lign and Plant for Experimental Dyeing of full-width calico, and the Calico-printing Laboratory a complete range of Full-size Machinery.

Prospectus and particulars free on application.

Ogilvie Duthie, Director of Education.

IMPORTANT NEW SCIENCE BOOKS.

MATERIALIEN DER STEREOCHEMIE. Ed. C. A. BISCHOFF. 2 stout vols., 8vo, covering the period from 1894 to 1902. £4 10s.

PAULI (Dr. R.)—DIE SYNTHES DER AZOFARBSTOFFE auf Grund eines symbolischen Systems. Large 8vo. £1 10s.

WOLFRUM (Dr. A.)—CHEMISCHES PRAKTIKUM. 2 vols. 8vo, and an ATLAS in folio containing 721 ill. and 11 plates. Cloth, £1 18s.

TRAITE DE CHIMIE MINERALE. Published under the Direction of HENRI MOISSAN, with the collaboration of the greatest Scientific Men. Vols. I. and III. To be completed in 5 vols. SUBSCRIPTION Price for the whole work, £3 9s., which will be raised Dec. 1, 1904. Any other BOOKS and PERIODICALS (English and Foreign) reviewed in this Paper promptly supplied.

A. OWEN & CO.,

English and Foreign Science Booksellers and Publishers.
298, HIGH HOLBORN, LONDON, W.C.

GERMAN CHEMICAL BOOKS

Rapidly and cheaply procured.

Catalogues gratis and post free.

W. MULLER,

59, Castle Street East, Oxford Street, London, W.

Laboratory and Yard for large or small scale Chemical and Metallurgical Work, with steam, electricity, &c., installed. Private office, and use of library and telephone. Owners would arrange reasonable terms for partial or sole use. Convenient situation, London—Address, "Box 31," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

BRYAN CORCORAN Lim.



MILLSTONE BUILDERS,
WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.

Sole Makers of MILBURN'S
Patent Conoidal Stone Grinding Mills.
Especially suitable for certain materials, Wet or Dry.

Works and Warehouses: Back Church Lane,
Farringdon Dept.: Basements of the Corn Exchange,
31, MARK LANE, LONDON.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC.
As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET
LEAD and PIPE, LITHARGE, SHOT, &c.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.
LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.

BATTERSEA POLYTECHNIC, S.W.Principal—SIDNEY H. WELLS, Wh.Sc., A.M.I.C.E., A.M.I.M.E.
Head of Department—JOHN WILSON, M.Sc.

SESSION begins on MONDAY, SEPT. 26th.

DAY and EVENING CLASSES in ORGANIC and INORGANIC CHEMISTRY (Theoretical and Practical) up to Hons B.Sc. (London)

SPECIAL COURSES in TECHNOLOGICAL CHEMISTRY, e.g., Paper Making, Paper and Pulp Testing, Gas Analysis, Assaying, Oils, Fats, Soaps, and Candles.

Complete Courses of Instruction (including Engineering subjects, German, Physics, &c.) for intending Works Chemists and General Analysts

The Laboratories are open for Research.
Prospectus gratis on application to the SECRETARY.
Detailed Prospectus 10s., post free 3d.

CITY OF LONDON COLLEGE,
WHITE STREET and ROPEMAKER STREET,
MOOKFIELDS, E.C.

MICHAELMAS TERM commences OCTOBER 3rd.

CLASSES and LABORATORY WORK in CHEMISTRY, PHYSICS, BIOLOGY, BOTANY, GEOLOGY, and PHYSIOLOGY. Special preparation for the Examinations of the Pharmaceutical Society, The Conjoint Board. Complete Courses for University Matriculation and Inter. and Final B.Sc., meeting during the Evening and on Saturday.

Full particulars gratis on application to—

DAVID SAVAGE, Secretary.

BIRKBECK COLLEGE,

Breems Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING ..	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board,
Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.

THE
DAVY FARADAY RESEARCH LABORATORY
OF
THE ROYAL INSTITUTION.

Directors:

The Right Hon. LORD RAYLEIGH, O.M., M.A., D.C.L., LL.D.,

SIR JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

Superintendent of the Laboratory:

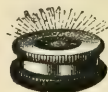
Dr. ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

This Laboratory was founded by Dr. LUDWIG
MOND, F.R.S., as a Memorial of Davy and Faraday, for the
purpose of promoting, by original research, the development and
extension of Chemical and Physical Science.

MICHAELMAS TERM.—Monday, October 3, to Saturday, December 17

LENT TERM.—Monday, January 9, to Saturday, April 15.

EASTER TERM.—Monday, May 8 to Saturday, July 22.

Full information and forms of application can be had from the
Assistant Secretary, Royal Institution, Albemarle Street, W.To prevent delay Candidates ought to send in their applications for
admission during the course of the Term preceding that in which
they wish to enter.**RADIUM BROM.****POLONIUM.****RADIO-ACTIVE ORES.****BAR.-PLAT.** CYAN. SCREENS.

" LARGE CRYSTALS.

ETC., ETC.,

ALL AT REASONABLE PRICES.

Armbrecht, Nelson & Co.,

71-73, Duke-st., Grosvenor-sq., W.

*Phone—4942 Gerard.

SECOND EDITION, NOW READY.

With Illustrations.

Price 2s. net (post free 2s. 1½d.)

Mdme. CURIE'S Thesis

ON

RADIO-ACTIVE SUBSTANCES.

REPRINTED from the CHEMICAL NEWS.

CONTENTS.

Introduction.—Historical.—Chap. I. Radio-activity of Uranium and Thorium; Radio-active Minerals.—Chap. II. Method of Research.—Chap. III. Radiation of the New Radio-active Substances.—Chap. IV. Communication of Radio-activity to Substances Initially Inactive.—Nature and Cause of the Phenomena of Radio-activity.

16, NEWCASTLE ST., FARRINGTON ST., E.C.

COVERS FOR BINDING.Cloth, Gilt-lettered Covers for Binding the Half-yearly
Volumes of the**CHEMICAL NEWS**

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered
at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

THE CHEMICAL NEWS.

VOL. XC., No. 2342.

THE ORIGIN OF RADIUM.*

By HERBERT N. McCOY.

THERE seems to be a tendency among chemists to divide radio-active substances into two classes. The permanently active substances, like uranium, thorium, and radium, belong to the first class, and those substances like uranium X, thorium X, the radium emanation, and polonium, whose activity is only temporary, to the second. The activity of the latter class disappears in some cases in a few minutes, and in others in the course of some months. In such cases it is supposed that the loss of activity represents the chemical decomposition or transformation of the active material. Some of the temporarily radio-active substances pass through two or more consecutive stages during their period of activity. Thus the radium emanation gives rise to the emanation X (formerly called "excited activity"), and thorium X gives rise to the thorium emanation. The different stages are experimentally distinguished by the amount of decrease of activity and by the penetrative power and deviability of the rays emitted. In each case the final product is an inactive product.

Only three elements are generally regarded as "permanently" radio-active—uranium, thorium, and radium. In the case of these the activity of a given mass seems to be constant. However, the methods of measuring radio-activity are not very exact, and the time of observation has at the most amounted to only very few years. Hence the direct experimental proof of the permanency of radio-activity is not conclusive. On the other hand, there exists an indirect proof that the activity of these elements is not strictly permanent, but only appears to be permanent because of the extremely slow rate of disappearance of the activity. This proof is of a three-fold nature. Firstly, it is almost indisputably proved that of the three kinds of rays emitted by radio-active substances, the α - and β -rays at any rate are of a material nature (Rutherford and Soddy, *Phil. Mag.*, 1903, [6], v., 576). If this is so, radio-activity is an attendant phenomenon, if not the result of the dissipation (transformation or decomposition) of the matter which forms the radio-active substance. Hence, it is not to be expected that a radio-active substance would possess perfectly constant activity. Secondly, uranium, thorium, and radium produce temporarily active substances, as has been mentioned already. The formation and decomposition of uranium X (Crookes, *Proc. Roy. Soc.*, 1900, lxvi., 409; Becquerel, *Comptes Rendus*, 1900, cxxi., 137) has been critically examined by Rutherford and Soddy (*Phil. Mag.*, 1903, [6], v., 441), who showed that the activity of UX decreases fairly quickly (to half the initial value in twenty-two days). They also made the very important discovery that UX is not an accidental impurity in uranium compounds, but is continuously produced from uranium. A uranium compound which had been freed from UX will, after some weeks, yield a new quantity of this product, which is practically equal in amount to that which was first removed. This process can apparently be repeated without limit. The rate of loss of activity of the UX is proportional to the remaining activity. The reaction is, therefore, according to the law of mass action, one of the "first order." It is a so-called "mono-molecular reaction." The observed rate of reproduction of UX in uranium is the same as we should expect if the UX was formed at a constant rate (proportional to the practically constant mass of the uranium), and was decomposed at a rate which is always proportional to its own mass.

In a perfectly similar manner thorium continuously produces the temporarily active substance, ThX (Rutherford and Soddy, *Phil. Mag.*, 1902, [6], iv., 381); radium gives first the radium emanation. This emanation, which is formed constantly and spontaneously (Rutherford and Barnes, *Phil. Mag.*, 1904, [6], vii., 202), seems to possess a gaseous nature. It is almost certainly of a material nature. This assumption has been practically indisputably proved by Ramsay and Soddy's discovery of fundamental importance, viz., that the final transformation product of the radium emanation is helium (*Nature*, 1903, lxviii., 354; *Zeit. für Physikal. Chem.*, 1904, xlviii., 490).

In all cases hitherto studied quantitatively it has been found that the transformations of the temporarily radio-active substances are reactions of the "first order." Although the activity of these secondary substances is considerable in comparison with the activity of the elements by which they were caused, yet the actual masses are in all cases exceedingly small. Nevertheless, this continuous product of discrete particles must be followed by a perceptible or complete transformation of the original substance.*

Finally, it is very probable that radio-activity is not the result of external excitation. Radio-activity does not decrease under the heaviest lead plates, and Elster and Geitel (*Weid. Ann.*, 1898, lxvi., 735) found in the case of uranium that at the bottom of a shaft 850 m. deep no loss of activity could be observed. It is hardly probable that any external excitation could penetrate the earth's crust to such a great depth undiminished in intensity. If, therefore, the assumption that the source of the energy of radio-active substances is internal (Rutherford, *Phil. Mag.*, 1903, [6], v., 576) is correct, we must hence conclude, according to our usual conception of the conservation of energy, that no radio-active substances can continually produce energy in undiminished amount.

These observations all lead to the conclusion that the activity even of the so-called permanently active substances must decrease in course of time, and most probably according to the same law which expresses the behaviour of the less permanent substances. Many estimates have been made of the amount of loss of radium, thorium, and uranium. Rutherford (*Phil. Mag.*, 1903, [6], v., 590) concludes that, in the case of radium, the loss amounts to about 0.001 of the total mass, and that the amount of the loss is 1,000,000 times as great as that of thorium.

If these estimates as such are rightly regarded according to their order of magnitude, it is clear that a comparatively short geological period would be sufficient for practically complete decomposition, and hence complete disappearance of radium from the earth, if this were present in relatively large quantities. On the other hand, the present existence of radium on the earth can be explained by the assumption that it is continuously produced from a substance itself decomposing much more slowly. Radium would then have the same kind of relation to this mother-substance as ThX to thorium, or UX to uranium.

Such a theoretical problem of chemical dynamics may be treated by a general method. Let a series of irreversible changes be assumed, which occur according to the following scheme:—



Let each change occur in an amount proportional to the mass of the changing substance, i.e., each change is of the first order. Let the velocity constants of the consecutive changes be K_a, K_b, K_c , &c. If then A represents the mass of substance A, $K_a A$ is the mass of B which is produced in unit time, $K_b B$, the mass of C, &c. Let now the mass of A be taken as constant. Then B will be produced with uniform velocity, $K_a A$. The mass B will thus increase till the amount of B, which is decomposed in unit time, is equal to that which is formed.

* With reference to this communication of Heydendorfer (*Phys. Zeit.*, 1902, iv., 81) concerning the loss of weight of an hermetically sealed tube of a radium compound, is of great interest.

* *Ber. der Deutsch. Chem. Gesell.*, xxxvii., 2641.

That is the case if $K_b B = K_a A$. The maximum value for B is therefore reached when—

$$B = \frac{K_a}{K_b} A \quad \dots \quad (1).$$

From this point the mass B will remain constant, as K_a and K_b are constants, and A was assumed to be constant. After the mass B has reached this constant maximum, C will have the same kind of relation to B as B to A. If equilibrium has ensued, it follows that $C = \frac{K_b}{K_c} B$. Similarly, $D = \frac{K_c}{K_d} C$, &c. By combining these equations we get $C = \frac{K_a}{K_c} A$, and, finally,—

$$N = \frac{K_a}{K_n} A \quad \dots \quad (2).$$

These equations show that in a series of irreversible processes of the first order, in the case of equilibrium the mass of each product is constant, assuming that the mass of the original substance was constant.

These equations only hold for conditions of equilibrium; general equations are readily obtained. The rate of formation of B is $K_a A$. The rate of decomposition of B is $K_b B$. The rate of increase of B is therefore $K_a A - K_b B$. Thus—

$$\frac{dB}{dt} = K_a A - K_b B \quad \dots \quad (3);$$

where t denotes the time. The integral of equation (3) for $B=0$, if $t=0$, is—

$$B = \frac{K_a}{K_b} A (1 - e^{-K_b t}) \quad \dots \quad (4).$$

If $t = \infty$ $e^{-K_b t} = 0$ and $B = \frac{K_a}{K_b} A$, as before, in the case of equilibrium.

Instead of a change of mass we can similarly consider a change of activity. The latter is, in fact, what is measured. Rutherford and Soddy (*Phil. Mag.*, 1902, [6], iv., 381) have shown that the amount of increase of activity caused by the formation of ThX in a thorium preparation, which had been freed from the former product, is expressed by the equation—

$$J_t = J_0 (1 - e^{-\lambda t}),$$

where J_t denotes the activity at time t and J_0 the activity when the maximum value of ThX has been reached. λ is a characteristic constant for this reaction. This equation differs from Equation (4) in that it expresses the maximum value of the variable by means of the experimentally determined value J_0 . Equation (4) is thus more general, in that it gives the magnitude of this maximum value in terms of two velocity constants, and in that of the mass (activity) of the mother-substance. The equation of Rutherford and Soddy also expresses the changes which occur with the formation of UX from uranium (*Phil. Mag.*, 1903, [6], v., 444), and that of the radium emanation from radium (*Phil. Mag.*, 1904, [6], vii., 202).

Equation 4 enables us to calculate the time which the product needs to reach a given fraction of its maximum value. For 99 per cent of the maximum it gives—

$$e^{-Kt} = 0.01,$$

and—

$$t = \frac{2 \times 2.3}{K} = \frac{4.6}{K} \quad \dots \quad (5).$$

For 99.9 per cent of the maximum it gives—

$$e^{-Kt} = 0.001,$$

and—

$$t = \frac{3 \times 2.3}{K} = \frac{6.9}{K}.$$

The time which any product requires to reach a practical maximum is thus inversely proportional to the velocity of

its decomposition. It should be found that a limiting value is practically reached in all cases in which the velocity of the decomposition of the product is very great in comparison with that of the mother-substance, as in all such cases the above mentioned condition, that the mass of the original substance must be constant, is practically fulfilled. If, moreover, in any series of products the velocity of decomposition of a certain product, N, is very small in comparison with that of a preceding product, we can calculate the time to reach the maximum of the product N, just as if this were a direct result, as the conditions of equilibrium of the intermediate products are reached in relatively negligible times.

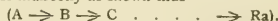
The Loss and Origin of Radium.

These considerations can now be applied to the case of radium. It has been shown that radium is probably decomposed at the rate of about one-tenth per cent per year. If this is correct, $K = 0.001$, if the unit of time is one year. By substituting this value in the equation $t = \frac{4.6}{K}$ we get $t \approx 4600$ years. According to this, the

amount of radium would have reached its maximum in all ores which are more than 5000 years old. From Equation

$$(1) Ra = \frac{K_1}{K} A, \text{ where } K_1 \text{ is the velocity constant of}$$

the decrease of the activity of the substance A whose decomposition either directly ($A \rightarrow Ra$) gives rise to radium, or indirectly as shown thus—



As has been previously mentioned, this condition will only actually exist if K_1 is very great in comparison with K . In this case A may be regarded as practically constant.

Now it is probable that most ores and minerals are much more than 5000 years old. According to the theory here propounded it would therefore be found that a certain relation exists between the amount of radium in an ore and that of the substance whose decomposition gave rise to the radium. The fact that radium occurs in many ores which also contain uranium seems to point to a genetic relation between the two elements. Moreover, uranium is also a radio-active substance which very probably decomposes, though, perhaps, extremely slowly in comparison with radium. If radium is actually a decomposition product of uranium it would be found that all uranium minerals contain radium in direct proportion to the uranium in them.

Moreover, all the intermediate products, such as UX or the subsequent products like the radium emanation, emanation X, &c., would also be present in amounts which are directly proportional to the percentage of uranium. Hence, it would be found that the total radio-activity of every natural uranium ore is directly proportional to the uranium it contains.

The fact that some uranium ores are considerably more radio-active than corresponds to the uranium in them led, as is well known, to the discovery of radium (P. and S. Curie and G. Bémont, *Comptes Rendus*, 1898, cxxvii., 1215). It was, however, an open question whether all ores would show an excess of activity.

In order to prove this hypothesis, a number of uranium ores from different localities were examined. Their radio-activity was measured by the electrical method, and their percentage of radium was determined. The results were in perfect agreement with the hypothesis. It was found that the activity of all uranium ores were free from appreciable amounts of thorium was directly proportional to the uranium they contained. The radio-activity of a given mass of any uranium ore divided by the percentage of uranium in the ore is constant. This constant may be called the coefficient of activity.

It has also been found that the radio-activity of uranium compounds prepared chemically is directly proportional to the amount of uranium they contain.

For such pure uranium compounds there exists also a

constant coefficient of activity. However, the magnitude of the coefficient of activity of all ores is more than five times as great as that of the pure salts. This excess in the activity of the ores is to be ascribed to the presence of radium in conjunction with the intermediate and decomposition products. The result is exactly that which we should expect if the above theory of the origin of radium is correct.

The Determination of Radio-activity.

For the determination of the radio-activity an aluminium leaf electroscope was used of the type which Hammer has described (*Trans. Am. Electrochem. Soc.*, 1902, iii., 316). It was charged by means of a battery. The earth connected metal case of the electroscope was connected with the positive pole of the battery. The plate connected with the aluminium leaf was charged by connecting with the negative pole. The position of the leaf was observed by means of a micrometer microscope whose scale had eighty divisions. The microscope was so adjusted that one end of the scale denoted a charge of about 115 volts and the other end 405 volts. For the measurements the electroscope was charged to about 240 volts. This threw the image of the little leaf off the scale. The time of the movement of the image over the eighty divisions of the scale during discharge was measured with a stop-watch which showed fifths of a second. The time of discharge through the eighty scale divisions thus amounted to about an hour if no radio-active substance was present. With 0.5 gm. of the purest ore the discharge took about fifteen seconds.

In order to determine the radio-activity of a specimen, 0.5 gm. of the finely powdered substance was distributed as evenly as possible over the bottom of a shallow round metal dish, which had a diameter of 7 c.m. The dish was placed with its contents underneath the square copper plate (5 sq. c.m.), which was connected with the aluminium leaf. The dish rested on a conducting support which was electrically connected with the earthed electroscope case. The amount of discharge depended on the distance of the copper plate from the dish (*Rutherford, Phil. Mag.*, 1899, [5], xlvii., 120). Table I. gives the times of discharge at different distances. The active substance was in each case 0.5 gm. of gummite.

TABLE I.

Distance in c.m.	Time in one-fifth second.	Mean.
8.0	97, 95, 98	97
5.9	83, 80, 83, 83	82
3.9	79, 80, 77, 78, 78	78
3.3	77, 78, 77	77
2.0	88, 87, 89	88
1.3	111, 108, 110	110

The greatest velocity of discharge was found at a distance of 3-4 c.m. In all subsequent measurements the distance amounted to 3.5 c.m. It may be seen from Table I. that the different determinations which were carried out under the same conditions did not differ from the mean by more than 2 per cent.

This represents about the degree of accuracy of the instruments employed. The times of discharge of feebly radio-active substances must be corrected on account of the spontaneous discharge of the empty electroscope. If t is the observed time of discharge for any substance and a the time if no active substance is present, the actual time of discharge θ , due to the active substance, is given by the equation—

$$\frac{t}{\theta} = \frac{1}{a} + \frac{\theta}{a - t}; \text{ whence } \theta = \frac{a \times t}{a - t}.$$

The value of a remains almost constant from day to day. Its mean value amounts to fifty-six minutes or 16,800 fifths of a second. The activity of a specimen is inversely proportional to the time of discharge θ . If the amount of uranium present is P , the coefficient of activity K is given by the equation—

$$K = \frac{1}{P \times \theta} \dots \dots \dots (6).$$

(To be continued).

ON THE CHANGES INDUCED IN THE PROPERTIES OF ELEMENTS BY VIEWING THEM UNDER OTHER EXTERNAL CONDITIONS THAN THOSE COMMON IN THE LABORATORY.

By GEOFFREY MARTIN, B.Sc. (Lond.).

THE human mind has an innate tendency to regard every quality and every quantity as discontinuous and unalterable.

For instance, our whole conception of number depends upon this mental peculiarity.

The vast mathematical fabric which has been erected upon the theory of equations ultimately depends upon the possibility of finding certain constants which will reduce certain algebraical expressions to zero—the so-called roots of the equation.

Another great branch of analysis, the invariant theory, depends upon the possibility of making these same mathematical expressions assume, not zero, but a constant value, in whatever way the variables are changed.

In science this tendency shows itself in a thousand ways. For example, we are always unconsciously endeavouring to find some rigid distinction between men and animals, animals and plants, and even between different races of men—distinctions which invariably break down as our knowledge increases.

In chemistry this human weakness is very marked. Chemists are ever, and vainly, attempting to attribute fixed and permanent characteristic constants to the different bodies which come under their hands.

For example, the boiling-points and melting-points of compounds were once assigned the proud position of invariable constants. Later, it was found that these are in reality not constant, but depend upon the external pressures to which the bodies are subjected. The colour of a compound was until lately thought to be an invariable characteristic.

Now, we know it alters with the temperature, becoming, as a rule, more intense with increase of temperature, and fading into whiteness at very low temperatures.

The metallic or non-metallic condition of an element is at the present time firmly believed by chemists to be a fixed and permanent characteristic, uninfluenced either by temperature, pressure, electric strain, or any other conceivable influence which can be brought to bear upon the element.

So that, because oxygen happens to be a non-metal, and sodium a metal, under those particular temperatures and pressures under which the chemist lives, is for him a sufficient reason for believing that oxygen will continue to remain a non-metal, and sodium will continue to remain a metal under every other conceivable physical conditions to which these two elements can be subjected—in my opinion an almost infinitely improbable contingency.

The atomic weight of an element is believed to be an absolutely unchangeable constant of an element; though why everyone should be so absolutely cocksure about this matter it is hard to say, because nobody has yet carried out very accurate weighings under temperature conditions greatly different from 18° C. In fact, no one knows anything about the matter.

We invariably find that as science advances these so-called constants are not really constants, but are variables which, under the conditions under which we live and work, are very nearly constant.

It may be gravely doubted whether any quality or any quantity associated with a body is really permanent and unalterable. When James Thomson proved that what was firmly believed to be an eternal and unchangeable constant of nature, namely, the melting-point of ice, was in reality a variable depending upon the external conditions of temperature and pressure, he caused in the scientific world a shock of surprise as great as could be caused at the

present time were some one to prove that the atomic weight of oxygen altered with the temperature and pressure.

What we intend to discuss in this article is the changeability or unchangeability of the properties of elements.

A chemist at the present time piously believes that the properties of an element, as described in the text-books, are fixed and unalterable characteristics of that element, principally, by the way, because he has never reflected on any other possibility.

Thus we read that chlorine combines vigorously with sodium, does not act on carbon, produces a very explosive compound with nitrogen, &c.; and the young student of chemistry learns painfully by heart the chemical peculiarities of O, S, N, &c., in the fond belief that they are eternal and unchangeable characteristics of those elements.

As a matter of fact, they are but the particular phase of properties which those elements exhibit under the conditions under which we live and work. Under other conditions their properties are entirely different. For example, we read that H and O gases, when heated together, combine with the evolution of heat and light to produce water. This is, however, only within a moderate temperature range. Did we happen to live at a temperature of 10,000° C., H and O would be described in the text-books as capable of existing together as a non-inflammable mixture, such as N and O gases at ordinary temperatures.

Carbon and silicon at ordinary temperatures are quite dead and inert. At a red or a white heat they wake up and become perhaps the most active substances known.

Fluorine at a very low temperature relapses into a state of chemical deadness, but at ordinary temperatures it sears the face like the vapour of white-hot steel. Nitrogen itself, so dead and inert as it appears to us, becomes a body of great chemical activity at high temperatures—inflaming, for example, in O at the temperature of the electric spark.

Chromium or iron, when made positive pole of an electric battery, assume the properties of a noble metal, like Pt or Au; made negative pole and they resume their ordinary properties (Hittorf, "Über das Verhalten des Chroms," *Zeit. für Electrochemie*, 1899, No. 1). Nitrogen, subjected to a silent electric discharge, becomes chemically active. Oxygen, under the same conditions, becomes enormously more active. Such examples can be multiplied indefinitely.

There are but two ways of regarding this matter:—Either the properties which elements happen to exhibit under ordinary conditions of temperature and pressure are unalterable, or they are not.

The evidence is, I think, overwhelmingly against the first view. The properties of an element do undoubtedly alter, and alter very considerably, according to the conditions under which it is viewed.

That the properties of an element should alter with the external conditions under which it is viewed is not very surprising when we consider that the chemical properties an element exhibits depends entirely upon the different forces with which it attracts the different kinds of atoms. And it is almost universally believed that the chemical force which an atom exerts on other atoms depends in some way or other upon the arrangement or motion of the electrons which it contains. If, then, we subject an atom to external strains, which alter the internal arrangement or motion of its electrons, then we alter at the same time the external attractive forces which the atom exerts on other atoms, and so alter the way it reacts chemically.

The temperature, electric field, probably pressure, medium, &c., are all influences which could conceivably affect the motion of the electrons within the atom, and thus affect the attractive forces of the atom.

In fact, we are probably not going too far when we suppose that the properties an element exhibits depend to a very great extent upon the external conditions to which it is subjected.

However this may be, it is certain that if we conclude that the chemical properties of an element do alter with the

external conditions, such as the temperature, then we must also conclude that there is some law, simple or complex, which regulates this change.

For the change must take place in some definite manner or other, whether that manner be complex or simple, since the element invariably returns again to its original condition when cooled to its original state.

Does there exist a simple law regulating this change? Will not a study of the behaviour of elements viewed under widely different temperatures and pressures bring to light as remarkable and undreamt of discoveries in the universe of atoms and molecules as did the observations of Kepler and Tycho-Brahe bring forth in the hands of Galileo and Newton in the universe of worlds and suns?

As a suggestion to be seriously considered in this connection, I venture to put forward the view that the properties presented by any element at ordinary temperature are only particular *phases or conditions* which can be assumed by other elements also under other and as yet unknown conditions, and that our notions of the rigidity and unchangeability of the properties of elements are completely false, and arise to a great extent because of the experimental difficulties of accurately studying the properties an element exhibits under temperature and pressure conditions very different from those which hold in the laboratory and on the earth.

Those to whom our suggestion appears most incredible are precisely those who are most ignorant of the remarkable changes which sweep over the properties of elements when viewed at high or low temperatures and in the electric field.

It should be remembered that men were once in precisely the same mental condition as regards their views of the liquid, gaseous, and solid states in which different substances find themselves when all are viewed under the same conditions of temperature and pressure, as are chemists at the present time as regards their conceptions of the different chemical states which elements find themselves in when all are viewed under the same external conditions.

Yet we all know now that the solid, liquid, and gaseous conditions of matter are only particular phases or conditions which can be assumed in succession by any substance by altering the external conditions of temperature and pressure under which it is viewed.

So also I suggest that the different chemical states which different elements find themselves in when all are viewed under ordinary conditions, are merely particular phases or conditions which any element can assume in succession by altering in an as yet unknown way the various external conditions under which elements are viewed.

It should, however, be remembered that the temperature and pressure exert a great influence on the physical state (*e.g.*, liquid, solid, or gaseous state) which a body finds itself in, because these are the influences which most affect particles of a molecular scale of magnitude.

But the change in the properties of elements depends upon the possibility of effecting matter when in a still finer state of division—the sub-atomic state of Crookes—and so would be most affected, not by the temperature or pressure, but by finer influences analogous to the temperature and pressure—"sub-temperatures" and "sub-pressures" we will call them.

In fact, just as different compounds have comparable temperatures and pressures, *i.e.*, temperatures and pressures which bring them into the same physical state, so also different elements may have comparable "sub-temperatures" and sub-pressures" which bring them into the same chemical states.

All this might appear at first sight very alarming, but it is not improbable. We are, in fact, upon the dawn of a new and grander chemistry than that which the older chemists contemplated.

Indeed, I think that it is undeniable that certain substances can be made to resemble each other more closely in properties, chemically and physically, even by the opera-

tion of such a coarse influence as the temperature. And doubtless a closer resemblance could be obtained by altering other variables simultaneously, such as the electric field, pressure, surrounding medium, &c.

Let us give some examples:

Oxygen and Sulphur.

O and S, viewed both at a common temperature, are in quite dissimilar chemical states. If, however, we view the O at ordinary temperature and the S at some 800—1000° C., the resemblance is greatly increased.

1. O and S, viewed both at ordinary temperatures, are in quite dissimilar physical states; the O is a very volatile gas, the S a solid. S viewed at, say, 1000° would become a volatile gas, just as O is at ordinary temperatures.
2. At ordinary temperatures the O molecule is O_2 and the S molecule is S_8 . If, however, we view the S at, say, 1000°, its molecules have the same composition (viz., S_2) as the O molecule at ordinary temperatures.
3. Oxygen is very much more chemically active than S, both being viewed at ordinary temperatures. At 1000° C. S is quite—nay, more—chemically active than O at ordinary temperature.
4. The majority of the compounds produced by S at ordinary temperatures have no analogies among O compounds.

For example, while H_2SO_3 and $H_2SO_3 \cdot SO_3$ are quite stable at ordinary temperatures, the corresponding O analogues are too unstable to exist. If, however, S be viewed at 1000°, these compounds would become quite as unstable as the corresponding O compounds at ordinary temperatures; SO_3 , H_2SO_4 , and H_2SO all decomposing at a red heat.

At lower temperatures, however, O would probably assume the same condition that S assumes at ordinary temperatures. Probably complex compounds of oxygen, corresponding to H_2SO_4 , SO_3 , &c., are capable of existing at lower temperatures.

Indeed, the allotropic modifications exhibited by S at ordinary temperatures would probably be paralleled by O at low temperatures. Even at ordinary temperatures two allotropic modifications (against some eight or nine known for S) of oxygen are known, viz., O_2 and O_3 . At still lower temperatures the number of these allotropic modifications will probably increase. The field of low temperature research is an unexplored world.

The Halogens.

The same appears to be the case with the halogens. Fluorine seems to be in the same chemical state at ordinary temperatures as Cl at a higher temperature. F, in fact, performs a great number of reactions at ordinary temperatures which Cl can not, but which it can when heated up.

For example, metallic Ur burns in F at the ordinary temperature, in Cl at 180°, and in Br at 210°. So that F behaves towards Ur at ordinary temperatures just as Cl at 180° and Br at a higher temperature. A similar relation appears in their behaviour with a vast number of other substances. It is, in fact, a general phenomenon.

So that by viewing simultaneously F at an ordinary temperature, Cl at about 180°, and Br at a higher temperature, we would make them all resemble each other chemically much more closely than by viewing them all simultaneously at a common temperature.

Notice that here again (as with O and S) those conditions which seem to render substances chemically more alike also render them physically more alike. For example, Cl and Br being at 180° and 210° as perfectly gasified as is F at ordinary temperatures. Viewed all at a common temperature, say, 0° C., this is not the case; F being a volatile gas, Cl an easily condensable vapour, and Br a liquid. It seems as if the same factors which determine

the chemical similarity of bodies also determine their physical similarity.

Oxygen and the Halogens.

Viewed all at a common temperature, hydride of oxygen, viz., H_2O , differs very widely in properties from the hydrides of chlorine, bromine, and fluorine, HCl, HBr, and HF. And presumably for the same reason that oxygen differs widely from chlorine, bromine, and fluorine when viewed at the same temperature.

If, however, we view the water at a high temperature and the haloid acids at ordinary temperatures, or the water at ordinary temperatures and the haloid acids at low temperatures, the resemblance between them is greatly increased, and presumably also the resemblance between O and the halogen under these conditions is greatly increased.

For example, viewed all at ordinary temperatures, we find that, though metals dissolve in HCl or HBr, evolving H and forming salts, they do not thus, as a rule, dissolve in water.

If, however, we view the acids at ordinary temperatures and the water at, say, 200—300°, we find both water and acids behave towards metals in the same way. In fact, water at 200—300° reacts with metals, evolving H and forming oxides in precisely the same way that HCl and HBr react with metals at ordinary temperatures, evolving H and forming chlorides and bromides.

Thus, although water at ordinary temperatures is a neutral substance, not reddening litmus, it seems (like HCl or HBr at ordinary temperatures) to become acid at a high temperature. For example, at 400° H_2O decomposes KCl, evolving HCl, just as H_2SO_4 decomposes it at ordinary temperatures.

Conversely, at low temperatures, HCl and HBr seem to react in the same way as H_2O at ordinary temperatures, becoming, like water, colourless liquids, incapable of reddening litmus, dissolving metals, or hydrolysing fats.

Notice that here again those conditions which bring water into a similar chemical condition as HCl or HBr also bring it at the same time into the same physical condition. For example, H_2O , viewed at ordinary temperatures, is a liquid, while HCl and HBr are gases. But water viewed at 300° is, like HCl and HBr at ordinary temperatures, a gas. Conversely, water at ordinary temperatures and the acids at low temperatures are all liquids. Now, these observations apply not only to the hydrides of O, Cl, and Br, but in general to their other binary compounds also; e.g., the metallic oxides are, as a class, more stable and less fusible and volatile than the corresponding chlorides and bromides, viewed all at the same temperatures.

If, however, we view the metallic oxides at a higher temperature than the corresponding chlorides and bromides, we tend more to equalise both their stability and their fusibility and volatility. We are, in fact, dealing with a general phenomenon common to the compound of O and H.

Upon what do the chemical properties of elements depend? Solely upon their chemical affinities. And their chemical affinities alter in relative strength and intensity as the temperature changes (and probably also with the pressure, electric field, &c.).

If, therefore, we can arrange to view two different and dissimilar elements, A and B, under two different sets of external conditions, so adjusted as to cause the affinities which A exerts to be equal or proportional to those which B exerts, we would solve the problem of making A and B chemically similar.

Whether this can actually be done or not is at present unknown. The facts we have quoted, however, are suggestive. In this connection let me mention still another possibility. If we can take advantage of the changes in the attractive force of elements caused by altering the external conditions under which they are viewed, and arrange to view simultaneously all the different elements of the Periodic System, each under a different set of

external conditions, each separate set of conditions being so adjusted as to make each of the elements thus contemplated attract the same radicles with the same (or with proportional) forces, and thus to make all the elements simultaneously chemically similar, then we would arrive at a means of unifying and simplifying the Periodic System in a way that has hitherto not been dreamt of. Chemists, here again, piously believe in the permanency and unchangeability of their Periodic Law. That it holds approximately under ordinary conditions of temperature and pressure is to them (if they have even considered the matter) a sufficient reason to make them believe that it will hold under *all* other conditions of temperature and pressure. This may be so; but in my opinion it is almost infinitely improbable.

The Periodic System, as it appears to us, is only a particular case of a general relationship which exists between the atomic weights and properties of elements. For it is the particular relation which appears between these quantities when all the elements are viewed at one particular common temperature and pressure, the particular common temperature and pressure being that under which we live, namely, about 18° C. and about 760 m.m. pressure.

But it is by no means necessary (apart from the question of the chemist's personal convenience) to view all the elements under the same conditions of temperature and pressure. If a simple relation appears when this is done then some relation will probably hold under whatever way the temperature and pressure are altered.

It is quite as probable as not that a very much more simple law would appear by viewing in the way we have suggested each particular element under a particular temperature and pressure, a definite law being supposed to regulate the temperatures and pressures under which the various elements are viewed.

For example, it is conceivable that we might make all the elements chemically similar, and thus get rid of the groups and series of the system. Or we might arrange the conditions so as to make a continual and progressive alteration of properties of the elements with increase of atomic weight, and thus again get rid of the Periodic nature of the relationship altogether.

However, this may be, it is certainly desirable that the Periodic Law should be viewed not only under atmospheric conditions, but also under a series of other temperature and pressure conditions and the law of variation found.

Indeed, as regards the various elements we are in a condition altogether analogous to that which the older chemists were in towards the various gases. For just as Boyle's law, $PV = \text{constant}$, is the law connecting the pressure and volume of gases, viewed at a constant temperature, so also the Periodic Law is the law connecting the atomic weights and properties of elements all viewed at a constant temperature. And just as Boyle's law is no longer true when the temperature is made to vary, but is a particular case of a wider law expressed by—

$$PV = RT,$$

so also the Periodic Law probably does not hold true when the temperature is made to vary, but is a particular case of a wider law, and probably a very simple law.

I have spent nearly two years studying the available data for comparing the elements and their compounds as they appear at high temperatures, with a view to tracing such a law. I have, however, failed to trace such a law, but strongly suspect that the heavy elements, such as Pb or Tl of a group of the Periodic System, are pictures of the chemical conditions which the lighter elements assume if viewed at a high temperature. So that at very high temperatures N and P would enter into a chemical condition, such as is presented by the heavier elements, Sb and Bi, of the same group, viewed at ordinary conditions, and that if viewed at still higher temperatures would enter into a radio-active condition, such as radium presents at ordinary temperatures (CHEMICAL NEWS, 1901, lxxxiii., 130; 1902,

lxxxv., 205—310). So that if we view the different elements of Mendeleeff's Periodic System, the lightest series at the highest temperatures, and the heaviest series at the lowest temperatures, we might in this way reduce to uniformity the Periodic System. According to the modern electron theory, increase of temperature should increase the atomic weight, because it increases the motion of the electrons which compose the atom.

Data is, however, wanting, and will be wanting for fifty years to come.

All these are dreams, speculations, what you will. Our knowledge of chemistry is yet in an embryo state, and we cannot say what is possible and what is not. Yet the reader should not scoff these dreams as incredible. They were suggested by a very intimate study of the facts now known, facts which the reader has probably never considered.

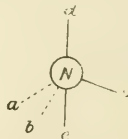
Let him remember that the dream of to-day is the living reality of to-morrow, and that coming events cast their shadows before them. The human mind is ever calling out for the new and unknown. The great labours of the atomic weight determinations were inspired and directed by the living underlying belief that some great and simple law would become apparent when we knew these constants more exactly. No man, for example, would have spent his life, as Stas did, in determining the atomic weights was he not borne up and sustained by the great theoretic interests underlying his observations.

University of Kiel.

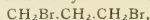
ON THE PENTAVALENT NITROGEN ATOM.*

By Professor OSSIAN ASCHAN.

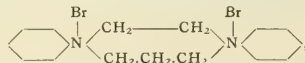
THE author has previously expressed the view (*Zeit. Phys. Chem.*, 1903, 46, 293), which is in accordance with that of van't Hoff ("Die Lagerung der Atome in Raume," 1894, 2te. Aufl., 136), that the valency directions of the pentavalent nitrogen atom are arranged as in the appended figure.



By the addition of trimethylene bromide,—



to ethylenedipiperide, $\text{C}_8\text{H}_{10} \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NC}_4\text{H}_9$, and of ethylene bromide to trimethylenedipiperide, $\text{C}_8\text{H}_{10} \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NC}_4\text{H}_9$, the author has obtained two stereomeric compounds having the constitution,—



which he was unable to resolve into optically active components by the aid of Pope's method with *d*-camphorsulphonic acid. Both compounds would therefore seem to possess symmetrical configurations, and this is only possible if the above conception of the arrangement of the valency directions of the pentavalent nitrogen atom is correct.

Since the attempts at resolution were carried out in aqueous solution, and as possibly the *d*-camphorsulphonic acid is not capable of effecting an easy separation of the stereoisomerides, the two ethylenetrimethylenedipiperide

* Read before the British Association (Section B), Cambridge Meeting, 1904.

dibromides were caused to react with silver *d*-bromocamphorsulphonate in absolute methyl alcoholic solution. Both gave highly crystalline ethylenedimethylene-dipiperidide *d*-bromocamphorsulphonates, which by crystallisation were separated into four and three fractions respectively, the fractions being then converted into the difficultly soluble iodide by precipitation with potassium iodide. The samples of iodide from the first and last fractions were then immediately examined polarimetrically, but were found to be optically inactive.

The author finds in these results a confirmation of his previously expressed views on the configuration of ammonium compounds, and notes also that this view possesses the greatest probability on grounds of a mechanico-chemical nature.

THE STEREOCHEMISTRY OF NITROGEN.*

By H. O. JONES, M.A., D.Sc.

THIS report, which was intended to form the basis for a discussion, contains a summary of the work which has been done on all branches of the subject, but deals more especially with the isomerism observed in quinquivalent nitrogen compounds.

The following is a brief *resumé* of the principal subjects discussed:—

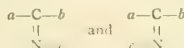
1. Tervalent Nitrogen Compounds.

The Problem of Optical Activity.—It might be expected from purely dynamical considerations that the most stable configuration for three atoms or groups attached to one atom (nitrogen) would be that in which all three groups were situated in the same plane with that atom. A displacement of one of the groups out of this plane might occur under certain circumstances, as, for instance, when strain is introduced by the formation of a double bond.

These conclusions are supported by experiment. The numerous attempts to obtain optically active tervalent nitrogen compounds, terminating with the experiments of Mr. J. P. Millington and the writer on compounds in which the valency of the nitrogen was not altered (from three to five) during the process, which have been unsuccessful; and the experiments of Messrs. Kipping and Salway, in which it was proved that the substituted acid amides produced by the interaction of an acid chloride containing an asymmetric carbon atom with various amines were homogeneous, and that therefore the nitrogen does not form a centre of asymmetry, afford fairly conclusive evidence of the plane configuration of compounds of the type *N.a.b.c.*

The existence of inactive isomerides is doubtful except in the case of tropine and tropylamine.

The well known isomerism of compounds of the type $\begin{smallmatrix} a \\ b \end{smallmatrix} > C = N - c$, illustrated by the oximes and hydrazones, is then briefly discussed. The very large number of experimental facts which have been collected since the discovery of the first isomeric benzil dioxime by Goldschmidt and V. Meyer in 1883 are accounted for in a satisfactory and consistent manner by the hypothesis of Hantzsch and Werner only. This hypothesis assumes that, in compounds in which a nitrogen atom is attached by a double union to another atom, there are two positions of equilibrium for the group attached to the third valency. The two isomerides being represented thus—



The consequences of the hypotheses have been fully verified for a large number of oximes and dioximes for hydrazones, aniles, and diazo compounds, but not for azo-compounds.

* Read before the British Association (Section B), Cambridge Meeting, 1904.

2. Quinquivalent Nitrogen Compounds.

Although a very large amount of work has been done on substituted ammonium compounds, the phenomena exhibited by them are so complicated, and in many respects so unlike those exhibited by asymmetric carbon compounds, that it is clear much more must be done before any definite conclusion can be arrived at.

i. *Compounds of the Type $N a_3 b X$* , where *a* and *b* represent mono-valent atoms or groups and *X* represents the acidic radical.

Isomerides of these compounds only exist in certain special cases in which *b* and *X* both contain an asymmetric carbon atom, observed by Professor Kipping and his collaborators. It has been conclusively proved that both *d*- and *l*-hydriindamine on combining with certain active acids, *d*-brom-camphorsulphonic acid, for example, give rise to two salts called *al* and *βl* and *al* and *βl* respectively; these salts combine to produce racemic compounds, which are very difficult to resolve. This isomerism is of theoretical importance, but is not of general occurrence, and it is evident that the discovery of the conditions determining the existence of these isomerides would throw much light on the phenomena observed in other quinquivalent compounds.

ii. *Compounds of the Type $N a_2 b c X$* have not been shown to exist in isomeric forms, though many attempts have been made by the writer and others to prepare them; but isomerism of a somewhat different kind has been observed by Aschan in the ethylene-trimethylene-dipiperidinium dibromides and diiodides.

iii. *Compounds of the Type $N a.b.c.d.X$* .—A very large number of compounds of this type have been prepared in all the possible ways, and though in some cases differences exist, these disappear on solution; no definite isomerism has been observed, except in one isolated instance, the *a*- and *β*-phenyl-benzyl-allyl-methyl-ammonium salts prepared by Wedekind. The very similar *p*-tolyl-benzyl-allyl-methyl, phenyl-benzyl-ethyl-methyl, and phenyl-allyl-ethyl-methyl ammonium compounds do not exist in definite isomerides.

Wedekind finds that isomerism apparently exists in some di-tertra-hydroquinolinium derivatives.

iv. *Optical Activity of Quinquivalent Nitrogen Compounds.*—Compounds of the types $N a_3 b X$ and $N a_2 b c X$ do not appear to be capable of giving rise to optical activity, while those of the type $N a b c d X$ can be resolved into optical antimers. The first compounds obtained in the active form were the *a*-phenyl-benzyl-allyl-methyl-ammonium compounds prepared by Messrs. Pope and Peachey. The basic ion was found to have a molecular rotatory power of about 166°. The writer succeeded in resolving phenyl-benzyl-ethyl-methyl-ammonium salts, and found the basic ion to have a rotatory power of about 19°; a series of compounds are being resolved by Miss M. B. Thomas and the writer with a view of investigating the remarkable effect of substitution on the rotatory power.

The analogy between asymmetric nitrogen and carbon atoms has been further extended by the writer by showing that when a tertiary amine containing an asymmetric carbon atom (methyl-*l*-amyl aniline) unites with an alkyl iodide (allyl and benzyl iodide) unequal quantities of the two possible compounds are produced.

v. *The Configuration of Quinquivalent Nitrogen Compounds.*—The existence of optical activity in substituted ammonium compounds shows that the compound is atomic, and has a spatial configuration which is devoid of a plane of symmetry.

The three principal configurations proposed, namely, the "cubic" of van't Hoff, the "double tetrahedral" of Willgerodt, and the "pyramidal" of Bischoff, are discussed in relation to the facts stated above. The tetrahedral configuration will not explain the existence of the isomeric hydriindamine salts, while both the cubic and tetrahedral configurations require, in general, a larger number of isomerides than the pyramidal. The pyramidal configuration is shown to be capable of accounting for all the known

facts, if it be assumed that during the addition of dX or HX to an amine, the acidic radical X takes up a position at the base of the pyramid, and is then capable of changing positions with the radical at the apex.

The existence of isomerism in compounds of the type $NabcdX$ in one case and its non-existence in all the other cases examined is difficult to explain, but possibly this depends on some peculiar relation between certain alkyl radicals, since hydrindamine salts with active acids behave similarly; that is, show sometimes isomerism and sometimes do not.

The existence and optical inactivity of the isomeric dipiperidinium compounds observed by Aschan is readily explained in a simple manner by the above view.

Reference must be made to the original for references and for the detailed discussion.

LUTES.*

By SAMUEL S. SADTLER.

(Concluded from p. 183).

VI. Resin, Shellac, and Wax.

A STRONG cement used as a stone cement is—

1. Resin	8 parts
Wax	1 part
Turpentine	1 "

It has little or no body, and is used in thin layers.

For nitric and hydrochloric acid vapours:—

2. Resin	1 part
Sulphur	1 "
Fire-clay	2 parts

Sulphur gives great hardness and permanency to resin lutes, but this composition is somewhat brittle.

Good waterproof lutes of this class are—

	Parts.
3. Resin	1
Wax	1
Powdered stone	2
4. Shellac	5
Wax	1
Turpentine	1
Chalk, &c.	8 to 10

For a soft air-tight paste for ground-glass surfaces:—

5. Wax	1
Vaseline	1

6. A strong cement, without body, for metals (other than copper or alloys of same), porcelain, and glass is made by letting 1 part of finely-powdered shellac stand with 10 parts of ammonia water until solution is effected.

VII. Rubber.

Because of its toughness, elasticity, and resistance to alterative influences, rubber is a very useful constituent in lutes, but its price makes its use very limited.

Leather cement:—

	Parts.
1. Asphalt	1
Resin	1
Gutta-percha	4
Carbon disulphide	20

To stand acid vapours:—

2. Rubber	1
Linseed oil	2
Fire-clay	3

Cement for mending rubber:—

3. Rubber, crude (sliced) ..	1
Resin	$\frac{1}{2}$
.. .. .	8

4. *Plain Rubber Cement.*—Cut the crude rubber in small pieces and then add the solvent. Carbon disulphide is the best, benzol good and much cheaper, but gasoline is probably most extensively used because of its cheapness.

5. To make corks and wood impervious to steam and water, soak them in a rubber solution as above; if it is desired to protect them from oil vapours, use glue composition (see Section IX.).

VIII. Linseed Oil.

This is one of the most generally useful substances we have for luting purposes, if absorbed by a porous substance that is inert.

Formulae:—1. China-clay } Of general utility for aqueous
Linseed oil } vapours.

2. Lime
Linseed oil } Forming the well known putty.

3. Red or white lead and linseed oil.

These mixtures become very strong when set, and are best diluted with powdered glass, clay, or graphite. There are almost an endless number of lutes using metallic oxides and linseed oil. A very good one, not getting as hard as those containing lead, is—

4. Oxide of iron and linseed oil.

IX. Casein, Albumen, and Glue.

These, if properly made, become very tough and tenacious; they stand moderate heat and oil vapours, but not acid vapours.

1. Finely-powdered casein	12 parts
Slaked lime (fresh)	50 "
Fine sand	50 "
Water to thick mush.	

A very strong cement for ground unions, stands moderate heat, as follows:—

2. Casein in very fine powder ..	1 part
Rubbed up with silicate of soda	3 parts

A strong lute for general purposes, which must be used promptly when made:—

3. White of egg made into a paste with slaked lime.

A composition for soaking corks, wood, packing, &c., to render them impervious to oil vapours, is:—

	Parts.
Gelatin or good glue	2
Glycerin	$\frac{1}{2}$ to 1
Water	6
Oil of wintergreen, &c., to keep from spoiling.	

X. Silicate and Oxychloride Cements.

For oil vapours, standing the highest heat:—

1. A stiff paste of silicate of soda and asbestos.

Gaskets for superheated steam, retorts, furnaces, &c.:—

2. Silicate of soda and powdered glass; dry the mixture and heat.

Not as strong, however, as the following:—

3. Silicate of soda	50 parts
Asbestos	15 "
Slaked lime	10 "

Metal cement:—

4. Silicate of soda	1 part
Oxides of metal, such as zinc oxide, litharge, iron oxide (singly or mixed)	
	1 "

* from the *Journal of the Franklin Institute*, clviii., No. 5.

Very hard and extra strong compositions :—

5. Zinc oxide 2 parts
Zinc chloride 1 part
Water to make a paste.
6. Magnesium oxide 2 parts
Magnesium chloride 1 part
Water to make a paste.

XI. Flour and Starch Compositions.

1. The well-known flax-seed poultice sets very tough, but does not stand water or condensed steam.
2. Flour and molasses, made by making a stiff composition of the two. This is an excellent lute to have at hand at all times for emergency use, &c.
3. Stiff paste of flour and strong zinc chloride solution forms a more impervious lute, and is more permanent as a cement. This is good for most purposes, at ordinary temperature, where it would not be in contact with nitric acid vapours or condensing steam.
4. A mixture of dextrin and fine sand makes a good composition, mainly used as core compound.

XII. Miscellaneous.

1. Litharge.
Glycerin.

Mixed to form a stiff paste, sets and becomes very hard and strong, and is very useful for inserting glass tubes, &c., in iron or brass.

For a high heat :—

2. Alumina 1 part
Sand 4 parts
Slaked lime 1 part
Borax ½ "

Water sufficient.

Of course, there are an almost infinite number of lutes or cements, but, classified as these are, they represent the largest number of them. The formulae that are not original, or were kindly given by friends, have been seen in the literature, one here and one there, and laid aside for a year or more, so I can hardly give the credit for them that I would like to.

A class of mixtures that can only be classified according to their intended use are core compounds.

1. Dextrin, about 1 part
Sand, about 10 parts
With enough water to form a paste.
2. Powdered anthracite coal, with enough molasses to form a stiff paste.
3. Resin, partly saponified by soda-lye 1 part
Flour 2 parts
Sand (with sufficient water) 4 "

(These proportions are approximate, and the amount of sand can be increased for some purposes).

4. Glue, powdered 1 part
Flour 4 parts
Sand (with sufficient water) 6 "

For some purposes, the exact uses of which I am not familiar, the following mixture is used. It does not seem to be a gasket or a core compound :—

5. Oats (or wheat) ground 25 parts
Glue, powdered 6 "

Sal ammoniac 1 part

I would say, in conclusion, that in any works or laboratory it is very good to have some such compositions made up ready to use without delay when wanted. Just which one, depends on the nature of the manufacturing or other work done.

I hope that the material contained in this paper may prove of benefit to some of my readers.

THE USE OF FERROUS SULPHATE IN THE ESTIMATION OF CHLORATES AND BROMATES.*

By I. K. PHELPS.

In a recent article, a method for the titrimetric estimation of nitric acid or nitrates was described (*Am. Journ. Sci.*, 1902, xiv., 440). It consisted, briefly, in the measurement of the amount of ferrous salt oxidised in the reduction of the nitric acid to nitric oxide by an excess of ferrous sulphate in the presence of hydrochloric acid. The value of ferrous sulphate as a reducing agent in analytical processes has long been recognised on account of its ready availability, the high degree of precision with which it may be determined, and the extreme slowness with which it is oxidised by atmospheric oxygen. This last fact was clearly shown by Peters and Moody (*Am. Journ. Sci.*, 1901, xii., 369) for solutions which had been allowed to stand until all active oxygen, dissolved in the water, or otherwise present, had produced its effect. The author was surprised to find that, in boiling such solutions in the open air and cooling with stirring in running water, no distinctly perceptible change could be noted, although the oxidation from day to day was plainly evident.

Carot (*Comptes Rendus*, cxviii., 449) has suggested the use of ferrous sulphate for determining the oxygen in hypochlorites and chlorates in admixture with chlorides, but gives no evidence to show the degree of accuracy of the process. Table I. records experiments made with the purest potassium chlorate of commerce to test this point. The dry salt was weighed out, treated with an excess of standardised ferrous sulphate solution (approximately $n/5$), and with 15 c.m.³ of sulphuric acid (1:4). This mixture was brought to the boiling-point in a trapped flask, cooled to room temperature by immersion in running water, diluted to a volume of 600 c.m.³, and, after the addition of 1–2 grms. of manganous chloride, titrated to colour with standard potassium permanganate solution.

TABLE I.

KClO ₃ taken. Gm.	Oxygen value of ferrous salt taken. Gm.	Oxygen value of ferrous salt found. Gm.	Error on KClO ₃ . Gm.
0.0500	0.02756	0.00814	0.00004
0.0500	0.02739	0.00781	0.00004 +
0.1000	0.04934	0.01024	0.00002 –
0.1000	0.04951	0.01043	0.00002 –
0.2000	0.09086	0.01247	0.00002 +
0.2000	0.09078	0.01277	0.00008 –
0.5000	0.20552	0.00993	0.00006 –
0.5000	0.20543	0.00980	0.00005 –

TABLE II.

KBrO ₃ taken. Gm.	Oxygen value of ferrous salt taken Gm.	Oxygen value of ferrous salt found Gm.	Error on KBrO ₃ . Gm.
0.0500	0.01776	0.00357	0.00006 –
0.0500	0.01770	0.00366	0.00001 –
0.1000	0.03792	0.00942	0.00008 –
0.1000	0.03792	0.00922	0.00001 –
0.2000	0.06321	0.00576	0.00003 +
0.2000	0.06321	0.00580	0.00002 –
0.5000	0.15670	0.01342	0.00001 +
0.5000	0.15212	0.01870	0.00008 –

Table II. records similar experiments made upon a sample of thrice crystallised potassium bromate which was prepared by acting on potassium hydroxide with bromine evolved from pure potassium bromide by sulphuric acid and manganese dioxide. The experiments were performed like those with the chlorate, described above, except that the

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, [4], viii., No. 99.

excess of ferrous salt used in the reduction was determined by decinormal iodine in alkaline solution instead of by permanganate in acid solution. The solution was cooled after boiling, was nearly neutralised with a concentrated solution of sodium carbonate, and was then treated with 2-3 grms. of Rochelle salt in solution and an excess of decinormal iodine solution. The mixture was made alkaline with an excess of potassium bicarbonate solution, starch paste added, the starch blue bleached with decinormal arsenious acid, and, finally, the excess of this last titrated to colour with iodine.

An inspection of the results shows that the processes may be justly considered as accurate for analytical purposes—especially so when one considers that they measure only the oxygen in the salt analysed, which is 39 per cent for potassium chlorate and 28 per cent for potassium bromate.

A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM, AND DIDYMIUM BY METANITROBENZOIC ACID.*

By ARTHUR C. NEISH.

THE work herein described was undertaken with the object of finding a shorter and more satisfactory method for the determination of thorium in monazite sands.

The requirements of such a method are—First, an accurate separation of thorium from cerium, lanthanum, and didymium; second, rapidity and ease of manipulation; third, an inexpensive reagent, and one which does not involve the use of alcohol.

It is believed that the method described meets these conditions.

As the analytical methods have been so recently reviewed by Metzger (*Journ. Am. Chem. Soc.*, 1902, xxiv., 901; *CHEMICAL NEWS*, lxxxvi., 218), and a bibliography to the entire literature of thorium recently published by Jouet (*Smithsonian Miscellaneous Collections*, No. 1374), the usual historical review of the literature pertaining to the subject is omitted.

Preparation of Pure Thorium Nitrate.

The pure thorium nitrate was made by dissolving 200 grms. of chemically pure thorium nitrate—containing a small percentage of cerium—in water in thirteen beakers, each holding about 1000 c.c. To each beaker 150 c.c. of hydrogen peroxide (Marchand's medicinal, containing about 4 per cent hydrogen dioxide) was added (10 c.c. for every 0.5 gm. thorium oxide). The solutions were heated to 85° C. and allowed to settle. The precipitates were washed by decantation, and at the end of the sixth decantation the filtrate gave no test whatever for cerium on the addition of ammonia. The precipitates were transferred to a large Büchner funnel and the washing continued, stirring the precipitate with a spatula. The precipitate was transferred to a large evaporating dish, and 250 c.c. of concentrated nitric acid added, which readily dissolved the precipitate when a little heat was applied. The solution was evaporated to dryness, taken up with water, diluted, and divided among the thirteen beakers so that each contained about a litre, and the thorium re-precipitated as before. The precipitate was dissolved in nitric acid and evaporated to dryness, and dried in the air-bath for three days at 115° C. This gave thorium nitrate of the highest purity, containing no free nitric acid.

Sixty grms. of this thorium nitrate were dissolved in 7 litres of water, well shaken, and divided among several well-stoppered bottles.

Standardising the Thorium Solution.

A very accurately standardised burette was used to measure out the thorium nitrate solution; it was connected to the bottle by glass tubing, so as to facilitate filling without any chance of change due to evaporation or contamination.

Different amounts of thorium solution were run into a number of small beakers and heated to boiling, and a boiling solution of oxalic acid (saturated in the cold) was added, a little at a time with constant stirring. After cooling, the precipitate was filtered and washed with water. If precipitated from cold solutions, the precipitate runs through the paper, but from hot solutions no trouble in filtering is encountered. The paper containing the thorium oxalate was placed in a weighed platinum crucible, gently heated with a Bunsen burner until dry and the paper charred, then the heat was increased and the oxalate changed to oxide; it was next heated by a blast-lamp for fifteen minutes, cooled, and weighed. Table I. gives the results.

Th(NO ₃) ₄ . C.c.	(COOH) ₂ . C.c.	Weight ThO ₂ . Grm.	ThO ₂ in 1 c.c. Grm.
25	20	0.1128	0.004512
25	20	0.1128	0.004512
50	40	0.2256	0.004512
50	40	0.2255	0.004510
50	40	0.2255	0.004510
50	40	0.2255	0.004510

Precipitants Tried.

Many organic precipitants were tried, mostly weak organic acids, in the hope of finding one that would give a sharp separation, and a precipitate which would filter quickly without the use of alcohol.

The results are briefly as follows:—

Gallic acid precipitates thorium quantitatively from a hot alcoholic solution as a flocculent slimy precipitate. Salts of cerium, lanthanum, and didymium are not precipitated.

Tannic acid precipitates thorium quantitatively, but cerium, lanthanum, and didymium are not precipitated.

Citric acid precipitates all from an acetone solution.

Salicylic acid precipitates thorium. The precipitate is soluble in excess of the reagent.

Oleic acid in a strong alcoholic solution precipitates thorium and cerium. The cerium precipitate is soluble in excess, the thorium insoluble.

Linoleic acid precipitates all, if insufficient alcohol is present, but with sufficient alcohol the cerium, lanthanum, and didymium readily dissolve; the thorium is apparently insoluble.

Paratoluic acid gave a precipitate of thorium, but none with cerium, lanthanum, and didymium.

Oxysiphthalic acid gave a white curdy precipitate of thorium in an aqueous solution, almost quantitatively; the other three earths gave no precipitate.

Benzoic acid precipitated thorium quantitatively from aqueous solution; the cerium, lanthanum, and didymium were not precipitated. This method gives trouble, on account of the very slight solubility of benzoic acid in water.

The three nitrobenzoic acids gave white precipitates with a neutral solution of thorium nitrate, while cerium, lanthanum, and didymium gave no precipitate. The meta acid, which is the most soluble in water, precipitated the thorium quantitatively. This acid is the principal product of the nitration of benzoic acid, the yield being about 75 per cent; but as the ortho- and para-acids, as well as benzoic acid, act similarly, it is not necessary to use pure metanitrobenzoic acid, and the reagent is one readily obtained.

Potassium iodate precipitates all four as heavy white precipitates.

* Read at the meeting of the New York Section of the American Chemical Society, May 6, 1904. From the *Journal of the American Chemical Society*, xxvi., No. 7.

Ammonium vanadate precipitates thorium, lanthanum, and didymium as canary-yellow precipitates; the cerium precipitate has an orange colour.

Lead acetate in a solution acid with nitric acid produces a white precipitate with thorium, which increases when heated, but is incomplete. Cerium, lanthanum, and didymium are not precipitated.

Arsenious oxide cream precipitates all four quantitatively in a solution containing sodium acetate.

Sodium tungstate precipitates all four as white precipitates.

Quantitative Precipitation of Thorium by Metanitrobenzoic Acid.

The solution of the precipitant is made by dissolving from 3.5 to 4 grms. of the acid in a litre of hot water (about 80° C.). When all is in solution, it is allowed to stand overnight, when a slight amount will separate out as feathery crystals. The solution is filtered to free it from any crystals and foreign matter.

Thorium nitrate solution was run into a 300 c.c. beaker and a solution of the precipitant added very slowly with constant stirring; about 150 c.c. gave a liberal excess for 25 c.c. of thorium solution equivalent to 0.1128 gm. of thorium oxide. This produces a heavy white precipitate, which soon collects on standing, more rapidly on heating. The beaker was heated on the water-bath to a temperature between 60° and 80° C. for fifteen minutes. The opalescence disappears, and the bulky precipitate settles to the bottom in large flocks having much the appearance of silver chloride. The solution can either be filtered hot or allowed to cool. The precipitate is washed first by decantation and finally on the filter-paper with a 5 per cent solution of the precipitant. The precipitate and paper are not dried, for reasons given later, but placed moist in a weighed platinum crucible and carefully heated with the cover off; then, after the paper and volatile matter are driven off, heated with the full flame of a Bunsen burner until white, then covered and ignited for fifteen minutes with the blast-lamp, cooled, and the thorium oxide weighed.

Table II. shows that thorium is quantitatively precipitated from a neutral solution of the nitrate by metanitrobenzoic acid.

TABLE II.

Th(NO ₃) ₄ .	Precipitant.	ThO ₃ found.	ThO ₃ taken.	Error.
C.c.	Gm.	Gm.	Gm.	Gm.
50	300	0.2256	0.2256	0.0000
25	150	0.1132	0.1128	+0.0004
36	150	0.1630	0.1625	+0.0005

(To be continued).

NOTICES OF BOOKS

Chemical Technology and Analysis of Oils, Fats, and Waxes. By Dr. J. LEWKOWITSCH, M.A., F.I.C. Third Edition. London: Macmillan and Co., Limited. New York: The Macmillan Company. 1904.

THE third edition of this valuable and compendious work has been enlarged to such an extent as to alter its form completely from that of the original, so that it represents practically a new work. The physical and chemical properties and the analysis of all known oils, fats, and waxes occupy the whole of the first volume, while the second is devoted to the chemical technology of oils and fats, manufacturing processes being discussed and in some cases illustrated, and the naturally occurring substances and their properties fully described. In the present form this work is undoubtedly the most complete on the subject in the language, and evidently every possible care has been taken to bring this edition up to date, and to make it quite indispensable to the technical chemist.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 10, September 5, 1904.

A Characteristic Reaction of Hydrogen Phosphide, Arsenide, and Antimonide.—P. Lemout.—Mercuric iodide, when dissolved in water in presence of potassium iodide, constitutes a very sensitive reaction, identifying the three gases PH₃, AsH₃, and SbH₃. In each case reduction takes place, and a very characteristic crystalline precipitate is formed of a yellowish orange, clear brown, or brownish black, of the type of mercury iodophosphide, PHg₃I₃, and whose formation can be easily demonstrated by a series of experiments. The reaction may be expressed by the equation $\text{PH}_3 + 3\text{HgI}_2 = 3\text{HI} + \text{PHg}_3\text{I}_3$.

Benzopinacone and Benzopinacoline.—Amand Valeur.—The author previously investigated the action of bibasic acid ethers, and particularly methyl oxalate on phenyl-magnesium bromide, C₆H₅MgBr. By the action of ethyl oxalate on phenyl-magnesium bromide W. Dilthey and E. Last obtained a substance fusing at 181°, but which could not be analysed, and which possessed all the properties of β -benzopinacoline. However, by applying the same reaction to methyl oxalate, the author obtains, not a benzopinacoline, but the benzopinacone, (C₆H₅)₂C(OH)—C(OH)(C₆H₅)₂.

No. 11, September 12, 1904.

This number contains no chemical matter.

IMPORTANT NEW SCIENCE BOOKS.

MATERIALIEN DER STEREOCHEMIE. Ed. C. A. BISCHOFF. 2 stout vols., 8vo., covering the period from 1840 to 1902. £4 10s.
PAULI (Dr. R.)—DIE SYNTHESE DER AZOFARBSTOFFE auf Grund eines symbolischen Systems. Large 8vo. £1 10s.
WOLFRUM (Dr. A.)—CHEMISCHES PRAKTIKUM. 2 vols. 8vo., and an ATLAS in folio containing 721 ill. and 11 plates. Cloth, £1 18s.
TRAITE DE CHIMIE MINERALE. Published under the Direction of HENRI MOISSAN, with the collaboration of the greatest Scientific Men. Vols. I. and II. To be completed in 4 vols. Subscription Price for the whole work, £3 5s., which will be raised Dec. 1, 1904. Any other BOOKS and PERIODICALS (English and Foreign) reviewed in this Paper promptly supplied.

A. OWEN & CO.,

English and Foreign Science Booksellers and Publishers.
280, HIGH HOLBORN, LONDON, W.C.

MELTING & BOILING-POINT TABLES.

BY

THOMAS CARNELLEY,

D.Sc. (Lond.), B.Sc. (Vict.), F.C.S.,

Professor of Chemistry in University College, Dundee.

The Standard and only work upon the subject.

2 Vols. Ry. 4to. 799 pp. 42s.

HARRISON & SONS, Pall Mall, London, S.W.

IMPERIAL

COLLEGE OF CHEMISTRY,
49 & 51, IMPERIAL BUILDINGS, LUDGATE CIRCUS, E.C.

Principal—FREDERICK DAVIS.

PRACTICAL AND THEORETICAL TUITION

In Botany, Chemistry, Pharmacology, and Therapeutics for All Medical and Science Examinations.

Special Course of Instruction in Therapeutics, Pharmacology, and Microscopy for Institute of Chemistry Exam.

To Chemical Manufacturers, Iron and Metal Merchants, and others.—Messrs.

FULLER, HORSEY, SONS, and CASSELL are instructed to **SELL by AUCTION**, at the Lea Chemical Works, Carpenters' Road, Hackney Wick, on **THURSDAY, Oct. 20**, at Eleven o'clock precisely.

CHEMICAL PLANT and MACHINERY, including about 60 tons of lead in tanks, coolers, vats, &c., enamelled iron baths, two pairs vacuum pumps, Johnson's air compressor, seven steam and other pumps, quantity lead and enamelled iron trays, pair of edge runners, three acid grinding mills, three sizers, two ranges of coke ovens, disintegrator, water softening apparatus, large quantity of tin, lead, and iron piping and cocks, aluminium trays, three w.i. water tanks up to 3000 gallons, about 30 tons c.i. floor plates, Tangies' 17-n h.p. horizontal steam engine, three smaller steam engines, two Lancashire boilers, 7 ft. and 7 ft. 6 in. diameter, 30 ft. long, two elephant b'lers, shafting and belting, steam winch, crab, 10 cwt. weighing machine, 7½ cwt. screw cutting lathe, four cranes, blocks, and chain, quantity stores and material, office furniture, and Effects.—May be viewed and catalogues had of Messrs. **KINGSFORD and DRAKE**, Solicitors, Bank Street, Ashford, Kent; and of Messrs. **FULLER, HORSEY, SONS, and CASSELL**, 11, Billiter Square, E.C.

Re Frederick Allen and Sons (Limited).—By Order of the Receiver for the Debenture Holders.

To Chocolate Manufacturers, Wholesale Confectioners, Manufacturing Chemists, Box-makers, Engineers, and others.—Messrs.

FULLER, HORSEY, SONS, and CASSELL are instructed to **SELL by AUCTION**, in Lots, on the Premises, Devon Wharf, Emmott Street, Mile End, E., on **TUESDAY and WEDNESDAY, Nov. 1 and 2**, at Eleven o'clock precisely each day.

MODERN CHOCOLATE PLANT and MACHINERY, including 14 grinding and mixing machines, five pairs French burr grinding stones, two pairs edge runners, three cocoa separating and dressing machines, two cocoa roasting machines, eight sets making and refining rolls, ten copper boiling and mixing pans, four caramel machines, five moulding tables, eleven rapping tables, twelve mould drying closets, two cream mixing machines, 15 covering tables, two furnaces, 17 runchas, four freezing chambers.

A COMPLETE REFRIGERATING PLANT, with two ammonia compressors and engines, two ammonia condensers, refrigerating and brine tanks, eight brine and other pumps, two Galloway boilers, a Green's economiser, two compound condensing beam engines, six horizontal engines, five steam pumps, shafting and gearing, driving bands, loose tools, utensils, and stock; immediately following the sale of the chocolate plant there will be sold the nearly new

BOX-MAKING PLANT and MACHINERY, at the Bell Wharf Box Works, adjoining, including twelve circular saw benches, band saw machine, seven panel, lighting, and hand-d planing machines, box perforating and printing machines, 15 Webster's box-nailing machines, three trimming machines, saw sharpener, hoop-iron punching machine, glue-heating apparatus, two horizontal steam engines, two pumps, tanks, shafting, &c.—May be viewed, and catalogues had of the Receiver, Mr. EDWARD H. FLETCHER (of Messrs. Cooper Bros. and Co.), Chartered Accountant, 14, George Street, Mansion House, E.C.; of Messrs. **BADDELEY and CO.**, Solicitors, 60, Leadenhall Street, E.C.; or of Messrs. **FULLER, HORSEY, SONS, and CASSELL**, 11, Billiter Square, E.C.

CHEMICALS, Pure and Commercial.

For Scientific and Technical Purposes

Specialities: **ETHERS, CHLOROFORM.**

POLGLASE & CO., Tyne Vale Chemical Works, Skinnerburn-rd., NEWCASTLE-ON-TYNE.



OLD PLATINUM

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and Purchased.

E. GEORGE & SONS,

BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.,

Are OPEN to PURCHASE Complete Sets

of short runs of the following:—*Chemical News*, *The Analyst Journal of the Chemical Society*, 1848 to 1850, *Journal of the Society of Chemical Industry*, or the Publications of any other English or foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.

RADIUM BROM.

Of 2,000,000 unit strength.

TWO TUBES of 5 Milligrams each
and **ONE TUBE of 2½ Milligrams.**

At £5 per mg. for cash.

Also a few Typical Specimens of the following:—

ÆSCHYNITE		SAMARSKITE	
Containing—	Per cent.	Containing—	Per cent.
Niobium oxide ..	22	Niobium oxide ..	56
Titanium ..	29	Iron oxide ..	15
Thorium ..	15.7	Uranium oxide ..	14 to 20
Cerium ..	18.4	Yttrium ..	8 to 11
Lanthanum ..	2.6	Thorium ..	6
Dydimium ..	2.6	Zirconium ..	4
Yttrium ..	1.1	And traces of Cerium, Calcium, &c.	

(URAL MOUNTAIN).

(URAL MOUNTAIN).

MONAZITE

LITHION GLIMMER

Phosphoric acid ..	28	Lithium oxide ..	2 to 5
Cerium oxide ..	37 to 45.7	Fluoric acid ..	4 to 8
Lanthanum oxide ..	27.4	Rubidium, Cæsium, Thallium, &c.	
Thorium oxide ..	18	(SAXONY).	
Traces of Calcium, Magnesium, Tin.			

(NORWAY).

At 3/6 to 4 - each.

ARMBRECHT, NELSON & CO.

71 & 73, Duke St., Grosvenor Square, W.

PLATINUM UTENSILS, SCRAP, LAMP ENDS, &c.,

Purchased at highest prices by—
DERBY & CO. LTD., 44, CLERKENWELL ROAD, LONDON.
N.B.—Platinum Sold.

BRYAN CORCORAN LIM.

MILLSTONE BUILDERS,

WIRE WEAVERS, MACHINE MANUFACTURERS AND GENERAL MILL FURNISHERS.

Sole Makers of MILBURN'S

Patent Conoidal Stone Grinding Mills.

Especially suitable for certain materials, Water Dry.

Works and Warehouses: Back Church Lane.

Factor's Dept.: Basement of the Corn Exchange.

31, MARK LANE, LONDON.

MICA

Telephone No. 2248 Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., & London

102 & 103, Minorities, E.C.,

MICA MERCHANTS.

Manufacturers of Mica Goods or Electrical and ALL purposes.

Contractors to His Majesty's Government.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGDON ST., E.C.

THE CHEMICAL NEWS.

VOL. XC., No. 2343.

THE ORIGIN OF RADIUM.*

By HERBERT N. MCCOY.

(Concluded from p. 189).

The Activity of Pure Uranium Compounds.

For the determination of the relation between activity and amount of uranium present two series of experiments were performed. In the first, intimate mixtures of a specimen of pure uranium acetate were prepared with finely powdered SiO_2 in the proportions of 1 to 1, 1 to 3, and 1 to 7. The activity of portions of $\frac{1}{2}$ grm. of each mixture, and also that of the pure salt, were determined. It was found that the time of discharge depended to a certain extent on the way in which the material was distributed in the dish. The greatest activity accompanied the most uniform distribution. Successive distributions of the same specimen, each as uniform as possible, give values often differing by 3–4 per cent. For this reason two or more distributions were usually made with each specimen, and the determination of the activity repeated. In the following statements the results of determinations with the same distribution are separated by commas (,) and the different distributions by semi-colons (;). The numbers denote the time (t) for the discharge of the electroscope through 80 scale divisions in fifths of a second. The corrected time, θ , was calculated by the help of Equation (6).

Pure uranium acetate:—478, 479, 480; 478, 476, 478. Mean 478. $\theta = 492$.

One part of uranium acetate to one part SiO_2 :—968, 994, 999; 956, 964. Mean 974. $\theta = 1034$.

One part of uranium acetate to three parts SiO_2 :—1850; 1904. Mean 1877. $\theta = 2110$.

One part of uranium acetate to seven parts SiO_2 :—3450. $\theta = 4340$.

Table II. gives the collected results. The value of K is in each case multiplied by the factor 10*.

TABLE II.

Parts SiO_2 to one part uranium acetate.	θ .	P.	K.
0	492	56	3'62
1	1034	28	3'45
3	2110	14	3'38
7	4340	7	3'29
Mean			3'44

The coefficient of activity, K, is nearly constant. The activity is practically proportional to the amount of uranium present.

In the second series, the activity of portions of $\frac{1}{2}$ grm. of different pure uranium compounds was determined. The descriptions of the specimens and the results obtained are given in the following:—

1. "Uranous Oxide Black" (Kny):—252, 251; 255, 260. Mean 255. $\theta = 259$.
2. "Uranous Oxide Black" (C. A. F. Kahlbaum):—267, 272; 263, 262. Mean 266. $\theta = 270$.
3. "Uranic Acid" (Kny):—290, 292; 308, 306. Mean 299. $\theta = 303$.
4. "Uranic Nitrate" (Kahlbaum, Kny):—637, 635; 617, 614. Mean 626. $\theta = 650$.
5. "Uranic Acetate" (Kny):— $\theta = 492$.
6. "Uranic Acetate" (Kahlbaum):—524, 525; 540, 524. Mean 528. $\theta = 545$.

* *Ber. der Deutsch. Chem. Gesell.*, xxxvii., 2641.

All these salts had been several years in the laboratory. They were thus old enough to contain the maximum of UXt (Rutherford and Soddy, *Phil. Mag.*, 1903, [6], v., 441).

Table III. gives the collected results.

TABLE III.

Number.	Formula.	θ .	P.	K.
1.	U ₃ O ₈	259	85	4'55
2.	U ₃ O ₈	270	85	4'37
3.	UO ₂ (OH) ₂	303	72	4'59
4.	UO ₂ (NO ₃) ₂ ·6H ₂ O	650	47	3'27
5.	UO ₂ (C ₂ H ₃ O ₂) ₂ ·2H ₂ O	492	56	3'62
6.	UO ₂ (C ₂ H ₃ O ₂) ₂ ·2H ₂ O	545	56	3'28
	Mean			3'86

The value of K is not perfectly constant. Two reasons can be given for this. In the first place the percentage of uranium used for the calculation of the value of K is the amount given by the usual formula. This is probably not the exact or even approximate value. Secondly, as the following pages will show, all uranium ores are more than five times as active, in comparison with the uranium they contain, as the chemically pure preparations.

Hence it follows that the process of purification more or less removes the strongly active adulterations. But as the degree of purity of the so-called pure substances differs in different cases, it is not remarkable that for this reason also the radio-activity shows some changes. This point thus requires further careful study. These results also illustrate the fact that the degree of absorption of radio-active rays by the same quantities of different substances is independent of the nature of the substance (Strutt, *Nature*, 1900, lxi., 531; see also Lenard, *Wied. Ann.*, 1895, lvi., 255).

Method of Analysis of Uranium Ores.

The determination of uranium is perhaps performed most quickly by reduction with zinc in dilute sulphuric acid and subsequent titration with potassium permanganate (Kern, *Journ. Am. Chem. Soc.*, 1901, xxiii., 685; Pulman, *Am. Journ. Sci.*, 1903, xvi., 229). The method is quick and fairly accurate. For the determination of uranium in pitchblende or gummitte, which contain iron, lead, calcium, and perhaps thorium as well as uranium, the ore is dissolved in warm dilute nitric acid and treated with a large excess of saturated solution of sodium carbonate (Patera, *Zeit. fur Anal. Chem.*, 1866, v., 228). After boiling for two minutes the precipitate, which contains all the iron, together with calcium, thorium, and the greater part of the lead, is filtered off. The filtrate, which contains all the uranium, is neutralised with sulphuric acid, and heated to drive off the carbon dioxide. The uranium is then precipitated as sodium uranate with sodium hydroxide, and the precipitate filtered off. This is then dissolved in dilute sulphuric acid, reduced with zinc, and titrated with permanganate.

The method here indicated for the separation of sodium uranate from pitchblende or gummitte is not applicable in the case of carnotite, an ore first described by Friedel and Cumenge (*Bull. Soc. Chim.*, 1899, [3], xxi., 328). This mineral is perhaps the uranium ore which occurs most abundantly in America (see Hillebrand, *Am. Journ. Sci.*, 1900, x., 135). Carnotite is chiefly a potassium uranium vanadate of unknown composition. Different methods for the separation of the uranium from the vanadium have been suggested, but none of them seem to be quite satisfactory (Hillebrand, *loc. cit.*). The methods of Friedel and Cumenge (*loc. cit.*) and of Ohly (*Journ. Amer. Chem. Soc.*, 1902, xxiv., 19) have been examined, but the separation was not complete in either case. A modification of the method of Langmuir (*Journ. Am. Chem. Soc.*, 1901, xxiii., 688) gave satisfactory results. Langmuir's method consists in precipitating vanadium as mercurous vanadate from a nitric acid solution neutralised by addition of mercuric oxide. An excess of oxide, however, may easily

give rise to the precipitation of some of the uranium. Hence the method was altered to avoid this difficulty. It was found that no uranium separated from a feebly acid solution of uranium nitrate, if a large excess of sodium acetate was added and the solution then boiled, but that by addition of sodium acetate and mercurous nitrate to a feebly acid solution of a vanadium salt, the vanadium was completely precipitated.

The method of analysis of carnotite finally employed is as follows:—A grm. of the mineral is dissolved in a small quantity of warm dilute nitric acid, and filtered from the insoluble residue after being diluted with water. The filtrate is almost, but not quite, neutralised with sodium hydroxide, and heated to boiling. A solution of about 1.5 grm. of mercurous nitrate is then added, and a solution of 3 grms. of sodium acetate. After boiling for a short time the precipitate of mercurous vanadate separates out, and is at once filtered. The excess of mercury in the filtrate is removed by means of sulphuretted hydrogen, and the uranium is determined in the usual way in the solution obtained, which is always found to be free from vanadium.

Composition and Activity of the Ores.

Altogether twelve different specimens of uranium ores were examined.

1. A piece of pitchblende of unknown origin, found in the laboratory collection. Specific gravity, 5.4. Analysis gave the following proportions:—Uranium, 61.1; U_3O_8 , 72.0; CaO , 8.0; PbO , 3.8; Fe_2O_3 , 2.5; Al_2O_3 , &c., 4.0; insoluble, 6.5; sum, 96.9. A considerable quantity of carbon dioxide was also found.

2. Pitchblende, Bohemia	41.5 per cent uranium.
3. " North Carolina	70.8 " "
4. " Colorado	59.1 " "
5. " "	16.7 " "
6. Gummite North Carolina	54.7 " "
7. " "	51.0 " "
8. Carnotite, Colorado	13.92 " "
9. " "	34.8 " "
10. " "	5.71 " "
11. " "	16.93 " "

The four last specimens were obtained from three different sources, Nos. 8 and 9 from the same.

12. Carnotite, Utah 1.6 per cent uranium.

The radio-activity of the ores was determined in the same way and under the same conditions as in the case of the pure compounds.

The numbers given as before the time in fifths of a second, which is necessary for the discharge of the electroscope through 80 scale divisions ($\frac{1}{5}$ grm. of the substance).*

1. 75, 72, 74; 71, 71, 71; 72, 74, 73. Mean 72. $\theta = 73$.
2. 113, 113, 112; 108, 106, 108. Mean 110. $\theta = 111$.
3. 56, 56, 57; 57, 57, 59. Mean 57. $\theta = 57$.
4. 81, 81, 81; 80, 81, 80. Mean 81. $\theta = 82$.
5. 247, 246, 251, 250; 237, 237, 238. Mean 243. $\theta = 247$.
6. 92, 92, 90; 89, 90, 89. Mean 90. $\theta = 91$.
7. 84, 82, 83; 82, 82, 81. Mean 82. $\theta = 83$.
8. 337, 343, 341; 330, 332, 332; 341, 340, 334. Mean 337. $\theta = 344$.
9. 150, 151, 152; 142, 145, 156, 153, 156; 148, 151, 151. Mean 151. $\theta = 152$.
10. 778, 765; 775, 772. Mean 773. $\theta = 810$.
11. 244, 238, 244; 237, 236, 240. Mean 240. $\theta = 244$.
12. 2320, 2315; 2322; 2311. Mean 2317. $\theta = 2693$.

* It was found that the activity of carnotite, which consists of quartz sandstone mixed with uranium, in the form of a coarse powder is greater than when it is finely powdered. This effect is due to the fact that in such ores the active substance forms a layer on the surface of the sand grains. If these grains are not ground up, an abnormally small absorption of the rays exist in the interior of the material on which the carnotite is deposited.

These results are collected in the following table:—

	θ .	P.	K.
1. Pitchblende	73	61.1	22.4
2. "	111	41.5	21.7
3. "	57	70.8	24.7
4. "	82	59.1	20.7
5. "	247	16.7	24.3
6. Gummite	91	54.7	20.1
7. "	83	51.0	23.7
8. Carnotite	344	13.92	20.9
9. "	152	34.8	18.9
10. "	810	5.71	21.6
11. "	244	16.93	24.3
12. "	2693	1.60	23.3

Mean 22.1

If we take into consideration the large experimental errors which the determination of θ involves, the values of K found for the activity are as constant as could be expected. The coefficient of activity of pure uranium salts is 3.86. The mean value for the ores amounts to 22.1. Hence the ores are 5.7 times as radio-active in proportion to the uranium they contain as the pure salts. Although this conclusion only rests on the study of a limited number of substances it undoubtedly represents a universal fact.

The assumption that radium is a decomposition product of uranium leads, as is shown above, to the conclusion that every uranium ore must contain uranium and radium in a definite proportion. If, then, the radio-activity of a substance is directly proportional to the amount of radio-active substance it contains (and it has been shown that this is the case for pure uranium compounds), the activity of every uranium ore should be proportional to the amount of uranium it contains; but the activity for equal amounts of uranium and equal quantities of substance in a definite proportion should be greater for the ore than for pure uranium compounds. This is exactly the result obtained experimentally. Hence it is probable that all uranium ores contain radium in amounts which are directly proportional to the uranium they contain.

We are further led to the conclusion that radium is one of the successive decomposition products of uranium. Thus the change occurs as far as is accurately known, according to the following scheme:—



There may also be other intermediate and final products.

From Equation 2 it follows that the amount of any intermediate product is inversely proportional to its rate of decomposition. In the case of radium this is very small in comparison with the rates for UX, RaEm, or EmX. Hence the actual masses of these latter substances, which are contained in uranium ores, are very small in comparison with the mass of the radium. The extensive occurrence of helium (Ramsay, Collie, and Travers, *Journ. Chem. Soc.*, 1895, lxvii., 684) in uranium ores is a further proof of the theory here put forward. The amount of helium contained in an ore will depend among other things on its degree of diffusion throughout the mineral. This degree will doubtless vary with the nature of the ore. The relative amounts of radium and uranium in ores can be estimated as follows:—The activity of radium (together with its maximum amount of radio-active products) is about 14 million times as great as that of uranium (plus the maximum amount of UX). The coefficient of activity of the ore is 5.7 times as great as that of the pure uranium compounds, and therefore in any ore the activity to be ascribed to the radium is 4.7 times as great as that of uranium. Hence it follows that one part by weight of radium is present in an ore to about 300,000 parts of uranium. If, for example, an ore contains 35 per cent of uranium it must contain 1 part of radium in a million. These calculated values agree well with the amounts actually found.

The radio-active intermediate products, as, for example,

thorium emanation, &c., are bodies which have little or no chemical affinity. It is uncertain whether they are to be regarded as compounds of the elements. Helium, the final product of radium, is destitute of all chemical properties. On the other hand, the chemical behaviour and spectrum of radium leave little doubt that it is an element belonging to the barium group. By the results here given an attempt has been made to show that an element, uranium, by its spontaneous decomposition produces another element, radium, which has a rather lower atomic weight, and possesses very well defined and decidedly different chemical properties. Such a transformation, if actually occurring, would afford a typical example of the theory of the genetic relation of the elements to one another as suggested by Thomson ("On the Structure of the Atom," *Phil. Mag.*, 1904, [6], vii., 237; see also Lengfeld, *Journ. Phys. Chem.*, 1901, v., 639).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1904.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, October 10th, 1904.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 204 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 204 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford during the month of September has been considerably below the average, only 1.26 inches of rain having been recorded. The average for September is 2.39 inches; we have, therefore, a deficit of 1.13 inches, which, if subtracted from the previous excess of 1.46 inches, leaves a total excess for the year of 0.33 inch, or 1.8 per cent above the thirty-five years' average.

Our bacteriological examinations of 382 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 382 others from special wells, standpipes, &c., making 764 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	138
New River, filtered (mean of 77 samples) ..	5
Thames, unfiltered (mean of 26 samples) ..	801
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 202 samples) ..	17
Ditto ditto highest	224
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	250
River Lea, from the East London District clear- water wells (mean of 26 samples) ..	7

Of the 305 daily samples taken from the general filter wells of the Metropolitan Water Board, twenty-five samples, or 8.2 per cent, were sterile. Eight samples, or 2.6 per cent, contained more than 100 microbes, and of these four samples contained more than 150 microbes per c.c. The eight excess samples contained an average of 159 microbes per c.c. In August eleven excess samples contained an average of 186 microbes per c.c.

The general results of the chemical and bacteriological examination of the various samples collected during September prove that the purity of the Metropolitan supply during the last month has not been equalled in recent years.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM, AND DIDYMIUM BY METANITROBENZOIC ACID.*

By ARTHUR C. NEISH.

(Concluded from p. 197).

Separation of Thorium from Cerium, Lanthanum, and Didymium.

THE next step was to try the separation of thorium from mixtures with cerium, lanthanum, and didymium, and then from mixtures of thorium with all three.

As before, known volumes of thorium nitrate solution were placed in beakers, known quantities of cerium, lanthanum, and didymium oxides added in the form of nitrates, then an excess of metanitrobenzoic acid was added slowly with constant stirring; the solutions were heated on the water-bath, filtered, and washed by decantation with a 5 per cent solution of the precipitant. The moist precipitate and paper were placed in a weighed platinum crucible, heated and ignited, with the precautions given above, and the thorium oxide weighed.

A separatory funnel with a capacity of 75 c.c. was found very convenient, both as a measure of the volume added and for adding the solution slowly while stirring.

The test for cerium in the filtrate by ammonia and hydrogen peroxide is of no use, as the metanitrobenzoic acid itself gives the same colour. The results given in Table III. show the efficiency of the separation.

These experiments showed that one precipitation will not separate thorium from an equal weight of cerium, lanthanum, or didymium, or from an equal or one-half the amount of all three. A nearly constant amount of each is carried down.

A re-precipitation being necessary, many methods were tried to change the thorium metanitrobenzoate to thorium nitrate. The precipitate is readily soluble in nitric acid, but on evaporating this solution a hard insoluble skin is left which encloses the impurities, making the second precipitation useless. The precipitate was dissolved off the paper into the precipitation beaker with hot dilute nitric acid (1 : 5), the paper well washed with hot water, the solution in the beaker diluted to about 150 c.c., and 25 c.c. of metanitrobenzoic acid added. Then methyl-orange was added until the solution became decidedly red, and then dilute ammonia (1 : 10) run in from a burette very slowly, with constant stirring, until the solution turns from deep red to light red or pink. The clear solution, after the addition of some ammonia, becomes opalescent, due to the re-precipitation of thorium metanitrobenzoate, and as more is added the

* Read at the meeting of the New York Section of the American Chemical Society, May 6, 1904. From the *Journal of the American Chemical Society*, xxvi., No. 7.

TABLE III.

Th(NO ₃) ₄ .	Precipitant.	Total volume.	Weight CeO ₂ .	Weight DiO ₃ .	Weight La ₂ O ₃ .	ThO ₂ taken.	ThO ₂ found.	Error.
C.c.	C.c.	C.c.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
25	150	175	0'1120	—	—	0'1128	0'1141	+0'0013
25	150	175	—	0'1120	—	0'1128	0'1140	+0'0012
25	150	175	—	—	0'1120	0'1128	0'1143	+0'0015
25	150	175	0'1120	0'1120	0'1120	0'1128	0'1199	+0'0071
25	150	175	0'1120	0'1120	0'1120	0'1128	0'1196	+0'0068
25	150	175	0'0560	0'0560	0'0560	0'1128	0'1162	+0'0034

TABLE IV.

25	150	175	0'0560	—	—	0'1128	0'1129	+0'0001
25	150	175	—	0'0560	—	0'1128	0'1131	+0'0003
25	150	175	—	—	0'0560	0'1128	0'1134	+0'0006
50	300	350	0'0560	0'0560	0'0560	0'2256	0'2263	+0'0008
26	150	175	0'1120	—	—	0'1173	0'1179	+0'0006
25	150	175	—	0'1120	—	0'1128	0'1129	+0'0001
25	150	175	0'1120	0'1120	0'1120	0'1128	0'1135	+0'0007

TABLE V.

25	150	175	0'5000	0'3000	0'2500	0'1128	0'1136	+0'0008
25	150	175	0'5000	0'3000	0'2500	0'1128	0'1137	+0'0009
25	150	175	0'5000	0'3000	0'2500	0'1128	0'1140	+0'0012
25	150	175	0'5000	0'3000	0'2500	0'1128	0'1136	+0'0008
25	150	175	0'5000	0'3000	0'2500	0'1128	0'1137	+0'0009
25	150	175	0'5000	0'3000	0'2500	0'1128	0'1136	+0'0008
25	150	175	0'5000	0'3000	0'2500	0'1128	0'1134	+0'0006

TABLE VI.

25	150	700	0'5000	0'3000	0'2500	0'1128	0'1126	-0'0002
25	150	700	0'5000	0'3000	0'2500	0'1128	0'1126	-0'0002
25	150	700	0'5000	0'3000	0'2500	0'1128	0'1125	-0'0003
25	150	900	0'5000	0'3000	0'2500	0'1128	0'1132	+0'0004
25	150	700	0'5000	0'3000	0'2500	0'1128	0'1123	-0'0005

TABLE VII.

	Th(NO ₃) ₄ .	Precipitant	Volume.	CeO ₂ .	ThO ₂ taken.	ThO ₂ found.	Error.
	C.c.	C.c.	C.c.	Grm.	Grm.	Grm.	Grm.
1.	25	150	300	0'0011	0'1128	0'1128	+0'0000
2.	25	150	300	0'0011	0'1128	0'1128	+0'0000
3.	25	150	300	0'0011	0'1128	0'1126	-0'0002
4.	25	150	300	0'0011	0'1128	0'1125	-0'0003

precipitate becomes white and flocculent, increasing as more ammonia is added.

When the precipitate becomes flocculent, the ammonia is added with great care, drop by drop, and the solution thoroughly stirred after every addition.

If the process of neutralisation were carried to the yellow tint, the other earths would precipitate.

The addition of ammonia is carried on until the red changes to pink; this marks the neutralisation of the mineral acid, and the weak acid (metanitrobenzoic) keeps the indicator pink. A very few drops more of ammonia would change the pink to yellow.

The solution of the precipitant changes methyl-orange decidedly red only when considerable quantities are added, and then the same depth of colour which mineral acids give is not produced. The 25 c.c. of metanitrobenzoic acid is sufficient to produce the pink.

At this point—the pink tint—all the thorium should be precipitated, but to ensure a complete precipitation 50 c.c. more of the precipitant are added, and the beaker heated on the water-bath as before, the solution filtered, and the precipitate washed with a 5 per cent solution of the precipitant, and either ignited and weighed or re-dissolved in nitric acid and the neutralisation repeated Table IV. shows the results with three precipitations.

The above results being satisfactory, the separation was tried on mixtures in the proportions usually found in monazite sands. Table V. shows the results with three precipitations.

It was thought that with greater dilution a closer separation could be obtained with two precipitations. Table VI. proves this to be the case.

The separation was next tried to see if one precipitation would separate thorium from cerium in the proportions in which they are present in Welsbach mantles. Nos. 3 and 4 were re-precipitated, giving slightly low results. (See Table VII.).

The Behaviour of other Elements.

Glucinum, gadolinium, yttrium, titanium, and samarium gave no precipitate, cold or hot.

Zirconium gave a white opalescence and precipitate, which increased on heating.

Erbium gave an immediate white curdy precipitate in the cold, with little change on heating; the precipitation is quantitative.

The following commoner salts were tried, although none are apt to be present in the analysis of monazite:—Calcium chloride, barium chloride, magnesium chloride, potassium-aluminium sulphate, potassium-chromium sulphate, ferrous sulphate, ferric sulphate, zinc sulphate, manganous sulphate, nickel nitrate, cobalt nitrate, bismuth nitrate, silver nitrate, lead nitrate, cadmium nitrate, copper nitrate, arsenious acid, arsenic acid, potassium-antimonyl tartrate (tartar emetic), ammonium molybdate, auric chloride, hydrochloroplutonic acid, ammonium tungstate, uranium nitrate, mercurous nitrate, mercuric nitrate, stannous chloride, and sodium stannate. With the exception of the last four, they gave no precipitate. The precipitates

with mercurous and mercuric nitrates were very heavy, white and curdy in the cold, but dissolved on heating.

Composition of the Precipitate.

The precipitate used for the determination of its composition was made by dissolving the pure thorium nitrate in water in a large beaker and precipitating with an excess of metanitrobenzoic acid. The precipitate, after heating on the water-bath, was washed by decantation, then on the filter, a Büchner funnel, with a large amount of water to make the washing complete. The precipitate was transferred in a cake to a glass plate, and dried for days in the air-bath at 115° C. When thoroughly dried, it was broken and pulverised, and again dried for two days, being frequently stirred so as to insure complete drying.

It was assumed that thorium would combine with 4 molecules of the acid as $\text{Th}(\text{C}_6\text{H}_4\text{NO}_2\text{COO})_4$.

The percentage composition calculated from this assumption is:—Th = 25.93 per cent; C = 37.46 per cent; H = 1.79 per cent; N = 6.26 per cent; O = 28.54 per cent.

The precipitate gave on analysis:—Th = 25.95, 25.97, 26.00, and 26.05 per cent; C = 37.43, 37.48, 37.32, and 37.12 per cent; H = 1.85, 1.85, 1.91, and 1.97 per cent; N = 6.42 and 6.48 per cent.

Properties of Thorium Metanitrobenzoate.

The precipitate, when dry, presents very peculiar properties; it is snow-white, very light, and is electrified. When pressed or touched with a glass rod or a brush it acts like pitch balls, being first attracted, then repelled by the rod, so that it is impossible to handle it without loss. Even the transfer of a precipitate to a platinum crucible cannot be accomplished without loss; for this reason, the precipitate is always ignited without previous drying. The thorium metanitrobenzoate is radioactive, giving, after an exposure of five days to an X-ray plate, a faint image, while the thorium oxide, produced from the ignition of the metanitrobenzoate, and the oxide separated from monazite sands by metanitrobenzoic acid, gave about four times the effect.

When thorium metanitrobenzoate is ignited, a large volume of gas is given off which burns with a sooty flame, leaving, after complete ignition, thorium oxide, snow-white and in a very loose condition. This oxide, when placed in a platinum boat inside a platinum combustion tube and strongly heated with two blast lamps, gave off white fumes, similar to those obtained by Metzger from the oxide obtained by the ignition of thorium fumarate (*Journ. Am. Chem. Soc.*, 1902, xxiv., 907). These fumes were collected in a small glass tube, but disappeared after a few minutes.

Thorium metanitrobenzoate is insoluble in water, it is easily soluble in, and prevented from precipitation by, hydrochloric, nitric, sulphuric, and acetic acids. Tartaric acid or tartrate dissolve the precipitate, from which solution the thorium cannot be precipitated either by ammonium hydroxide, potassium hydroxide, or oxalic acid. Oxalic acid dissolves the precipitate with the formation of a white, crystalline precipitate of thorium oxalate. Sodium carbonate decomposes the precipitate with the production of a flocculent precipitate, soluble in excess of sodium carbonate. Potassium hydroxide decomposes it with the formation of thorium hydroxide. It is soluble in acetone; alcohol and ether have no solvent effect.

Monazite Analysis.

The practical application of the precipitation of thorium by metanitrobenzoic acid was applied to the analysis of monazite sands. The results were checked against the two shortest and best methods, the combination method and the fumaric acid method of Metzger (*loc. cit.*). Five sands were analysed, three from Brazil and two from North Carolina.

Fumaric Acid Method.

Metzger's method was used except for the following modification: The precipitate of thorium fumarate was

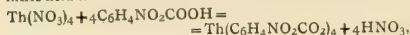
dissolved in hot, dilute nitric acid (1 : 5) instead of hydrochloric acid, and instead of evaporating to dryness, which produces a compact residue incompletely soluble in water, the thorium and other contaminating earths were precipitated as hydroxides, with an excess of potassium hydroxide, and the hydroxides filtered off, washed and dissolved in hot, dilute nitric acid (1 : 5), evaporated to dryness, taken up with 40 per cent alcohol, and precipitated with fumaric acid, as before; filtered, washed, ignited, and weighed as thorium oxide. This modification eliminates any chance of the other earths being enclosed in the insoluble residue on evaporation, and also any possibility of the thorium oxide being contaminated by silica.

Metanitrobenzoic Acid Method.

Two grms. of the sand were ground to a fine powder and weighed out into a porcelain crucible, about 10 to 15 c.c. of concentrated sulphuric acid added and stirred with a small glass rod, which is left in the crucible throughout the digestion. The crucible was placed on a hot plate, heated gradually and stirred cautiously to allow the escape of bubbles of gas, which are only formed at first, and cause loss if the heating is not done carefully. The heat was increased, or the crucible moved to the hotter part of the plate until a constant cloud of sulphur trioxide was given off. When the excess of acid had evaporated, more acid was added, the contents were stirred with the glass rod and the digestion was continued. As a rule, the digestion lasted all day, since the solution of the sulphates in water was allowed to stand over night, but two results are given where the digestion lasted only three hours, so that longer digestion is unnecessary. At the end of the digestion the phosphates present in the monazite sand were all changed to sulphates; the crucible now contained about 10 c.c.; this was well stirred, and, after cooling the crucible in ice water, the mass was allowed to drop from the rod, a drop at a time, with constant stirring into a beaker containing 600 c.c. of water cooled to 0° . After all the liquid was added, the crucible itself was placed in the beaker, and the whole allowed to stand, best over night. If it is a refined sand and free from quartz, the residue on the bottom of the beaker should be small, but if there is a flocculent precipitate, it is apt to be hydrated sulphate of thorium. In this case the best thing to do is to start another portion, using greater care in adding the mass to the ice-water and to have enough free acid present to make the mass liquid enough so that when a drop of it is added to the beaker it soon dissolves, leaving a fine white powder instead of sinking to the bottom as a hard lump, as it will do if too little acid is present.

The solution was filtered into a large beaker and heated to boiling. A boiling solution of oxalic acid (saturated in the cold) was added gradually to the solution with constant stirring, a large excess being used in order to make the precipitation complete in presence of so much sulphuric acid, and also to take any zirconium into solution, which would be precipitated by the metanitrobenzoic acid; an excess can have no solvent effect whatever on the thorium present. The solution was allowed to stand, and when cool, the white crystalline precipitate, consisting of the oxalates of thorium, cerium, lanthanum, and didymium, was filtered and washed with a dilute solution of oxalic acid. It is better to allow the precipitates of the oxalates to stand many hours, or, if possible, over night. The precipitate and paper were transferred to the precipitation beaker, 10 to 15 grms. of stick potassium hydroxide added, 25 to 50 c.c. of water, and the whole heated to boiling, washing down any oxalates that were attached to the sides of the beaker. The oxalates were soon changed to hydroxides, having a silky appearance and becoming yellow on account of the oxidation of the cerium. The solution was diluted to about 300 c.c., filtered and washed with water until free from alkali. The hydroxides were dissolved into the precipitation beaker with hot dilute nitric acid (1 : 5). This solution of the nitrates was evaporated to dryness on the water-bath, moistened with

water and evaporated until every trace of free nitric acid was driven off; since the precipitate is soluble in dilute nitric acid and as nitric acid is set free in the reaction,—



all free nitric acid must be removed from the nitrates.

The nitrates were dissolved in 500 to 600 c.c. of water and 150 to 250 c.c. of metanitrobenzoic acid solution added slowly with constant stirring, and heated on the water-bath at 60° to 80° until the precipitate has all collected and settled to the bottom. It was then filtered, washed by decantation, using a 5 per cent solution of the precipitant, then placed on the filter and washed with the same solution. The precipitate was dissolved by hot dilute nitric acid (1:5) into the precipitation beaker, the paper well washed with hot water and diluted to 600 c.c.; methyl orange was added until a decided red colour was produced, then 25 c.c. of metanitrobenzoic acid. This was neutralised with dilute ammonia (1:10) until a pink tint was obtained. This is best done by placing beside the beaker another containing the same volume and amount of acid and indicator, also containing some white powder, such as pulverised quartz, and frequently stirred during the titration to give the same appearance as the contents of the other beaker. As the excess of nitric acid is neutralised, the thorium re-precipitates as metanitrobenzoate, and the solution changes from a decided red to a pink colour, due to the feeble acidity of metanitrobenzoic acid. After the pink tint was obtained, 50 c.c. more of metanitrobenzoic acid were added to insure complete precipitation. The beaker was then heated on the water-bath to from 60 to 80°, the precipitate filtered, washed, and the wet precipitate ignited and weighed, after treating for fifteen minutes with the blast-lamp.

In the analysis of monazite some difficulty was experienced in obtaining a white thorium oxide, and also in the process of neutralisation, for in making the second precipitation rapidly some experience is required to catch the proper end-point. To obviate this the following modification was used, which, though a little longer, is much easier to carry out, and insures concordant results and a pure white oxide.

After the first precipitate of thorium metanitrobenzoate was dissolved in nitric acid, instead of neutralising with

ammonia, the thorium is precipitated as hydroxide by potassium hydroxide. The potassium hydroxide at first causes a re-precipitation of the flocculent metanitrobenzoate, but a slight excess changes it to hydroxide; this is easily seen by the change from a very voluminous white precipitate to a more compact cream-coloured one. The solution was then diluted and filtered through the same paper, washed and dissolved with hot, dilute nitric acid (1:5) into the same beaker, and evaporated to dryness, dissolved in 600 c.c. of water and precipitated with metanitrobenzoic acid, and the moist precipitate ignited, and the resultant thorium oxide weighed.

This modification is recommended, as it requires no experience with the use of the indicator, and if the preceding directions are carefully carried out, a snow-white oxide will always be obtained.

Conclusions.

1. Metanitrobenzoic acid precipitates thorium quantitatively as $\text{Th}(\text{C}_6\text{H}_4\text{NO}_2\text{CO}_2)_4$ from a neutral solution of the nitrate.

2. When this precipitation is repeated, it affords a complete separation from cerium, lanthanum, and didymium.

3. This method gives as good results for thorium in monazite as the combination or fumaric acid methods, and has the advantage in that it is much shorter, and offers no difficulties in precipitation or filtration; the precipitant is not expensive and avoids the use of alcohol.

This investigation was carried out under the direction of Professor Edmund H. Miller, and I wish to gratefully acknowledge my indebtedness to him for his kind interest and advice.

THE DETERMINATION OF MOLYBDENUM IN STEEL AND IN STEEL-MAKING ALLOYS.*

By FREDERICK VAN DYKE CRUSER

and
EDMUND H. MILLER.

INTRODUCTION.

As there is difficulty in obtaining an accurate and rapid estimation of molybdenum in steel and in steel-making alloys, the following work was undertaken in order to compare the best methods now in use. It was also the object of the investigators to point out the reasons for the discrepancies in the several methods, and, if possible, to devise a rapid and accurate method which will not be affected by the impurities in molybdenum steel, or by the other metals which are sometimes added, or may in future be added. The impurities are silicon, phosphorus, sulphur, manganese, and copper; metals added are molybdenum, tungsten, chromium, and those which may in future be added are uranium and vanadium.

PART I.

In making a determination of molybdenum in steel and in steel-making alloys, the main difficulty is the separation of molybdenum from iron.

There are two general methods for this separation. The first, and most commonly used, is to separate the iron from the molybdenum as ferric hydroxide, and the second is to separate the molybdenum from the iron as sulphide of molybdenum.

After the separation of the iron the molybdenum may be determined by three different methods. First, by reduction and titration with potassium permanganate; second, precipitation of the molybdenum as lead molybdate; third, by weighing the molybdenum as molybdenum disulphide. There are several other means of estimating molybdenum, but they do not seem to merit extensive consideration;

TABLE VIII.—Results on Monazite Sands.

	Metanitrobenzoic.	Modified metanitrobenzoic.	Fumaric.	Combination.
Refined Brazil monazite* ..	5'70 5'80 5'93 —	5'70 5'67 5'65 5'73 5'60	5'70 — — —	5'63 — — —
North Carolina monazite ..	5'48 5'12 —	5'27 5'26 5'27	5'13 — —	5'39 — —
Brazil monazite {	4'89 4'97 5'04	4'99 4'98 4'82	4'85 — —	4'90 — —
High-grade North Carolina monazite†	6'04 6'15 5'88	6'02 6'04 5'88 6'15	5'89 — — —	5'98 — — —
Refined Brazil monazite† ..	— —	5'81 5'71	5'71 —	5'97 —

* It was through the kindness of Mr. Whitaker, of the Welsbach Light Co., that these samples were obtained.

† From the original sample received from Professor Baskerville, not the same as used by Metzger (*Journ. Am. Chem. Soc.*, 1902, xxiv., 901). The digestion for these lasted three hours.

* Read at the meeting of the New York Section of the American Chemical Society, January 8, 1904. From the *Journal of the American Chemical Society*, xxvi., No. 6.

therefore, in comparing the different methods now used for analysing steel for the molybdenum content, the separation of molybdenum and iron will first be considered, and then the estimation of the molybdenum.

In order to test the efficiency of these two separations it was thought advisable to conduct a large number of experiments on solutions of pure salts, made up with varying proportions of iron and molybdenum. In beginning the work, two burettes were standardised against a standard 2 c.c. pipette; 7 litres of potassium permanganate solution were made up approximately N/10, filtered and standardised against pure iron ammonium sulphate, and against pure oxalic acid, the results agreeing. About 1 grm. of iron ammonium sulphate was used for the titration, and 0.3 grm. of oxalic acid, the titrations being made in duplicate. A solution of ferric chloride was made up, containing approximately 50 m.grms. of iron per c.c. This solution was standardised against the standard potassium permanganate solution. Four litres of a solution of ammonium molybdate were then made up, containing approximately A blank consisting of asbestos, water, and the same 5 m.grms. of molybdenum per c.c., and the strength of the solution determined.

As the accuracy of all the subsequent results depended upon the accuracy or the molybdenum content in this solution, it was necessary to standardise by different methods, and to have them checked.

Conditions for Precipitating Molybdenum as Lead Molybdate (Ibbotson and Brearley, "Analysis of Steel Works Materials," p. 275).—A number of determinations of the molybdenum were made, precipitating the molybdenum as lead molybdate under the following conditions:—

To 30 c.c. of the molybdate solution (containing about 150 m.grms. of molybdenum) a few drops of ammonia were added, and then 2 to 3 c.c. of acetic acid (33 per cent) in excess. The solution was diluted to a volume of from 200 to 250 c.c. and 4 to 5 grms. of ammonium chloride added; the solution was heated to boiling, and while boiling 45 to 50 c.c. of a lead acetate solution (40 grms. of crystallised lead acetate per litre) were added, then boiled for from two to four minutes, with vigorous stirring. The precipitate was allowed to settle, filtered through asbestos in a Gooch crucible, using suction, and washed by decantation with boiling water containing about 5 grms. of ammonium chloride in 200 c.c. and a few drops of acetic acid, until free from lead, the wash-water being tested with hydrogen sulphide. In washing by decantation, the washing solution was kept as hot as possible, and the solution stirred thoroughly before allowing the precipitate to settle. When free from lead, the precipitate was washed once or twice with boiling water. The Gooch crucible was heated on an asbestos plate until dry, then with the free flame, allowed to cool in a desiccator, and weighed.

Results.

Molybdate solution taken.	Weight of lead molybdate found.	Weight of molybdenum found.	Molybdenum per c.c.
C.c.	Grm.	Grm.	Grm.
30	0.5644	0.14765	0.004915
30	0.5655	0.14793	0.004931
35	0.6614	0.17302	0.004943
35	0.6579	0.17211	0.004917
40	0.7514	0.19657	0.004914

Not more than 3 c.c. of acetic acid should be added, as a large excess of acetic acid has a solvent effect upon the lead molybdate. Under these conditions the precipitate was granular, settled quickly, and filtered easily.

In order to check the results obtained by this method several others were employed.

First, precipitation of the molybdenum in an acid solution by hydrogen sulphide, at a temperature of 80° C. After an hour the solution was filtered and the filtrate re-treated as before. This was repeated four or five times, and a little more sulphide was obtained each time. The

precipitation under these conditions is incomplete unless repeated several times, as stated by Rose ("Traité Complet de Chimie Analytique Analyse Quantitative," 1862, p. 490), although used by Dohler in his method for analysing steel (CHEMICAL NEWS, 1900, lxxxii., 294). The molybdenum was then precipitated as molybdenum trisulphide in a sulphuric acid solution with hydrogen sulphide under pressure. The precipitation was complete, as stated by Treadwell, and was carried out as follows ("Kurzes Lehrbuch der Analytischen Chemie," vol. ii., p. 183):—200 c.c. of water at the room temperature, containing 10 c.c. of concentrated sulphuric acid, were saturated with hydrogen sulphide, and added to the molybdate solution in a pressure bottle. The pressure bottles used were the ordinary citrate of magnesia bottles, of about 350 c.c. capacity. After adding the solution, hydrogen sulphide was passed through until the precipitate collected; the bottles were then closed, placed in a water-bath, and heated at 100° C. for from one to two hours; after cooling, the sulphide was filtered on a Gooch crucible, and washed by decantation with water containing sulphuric acid (1:50) saturated with hydrogen sulphide. The sulphide was then converted into oxide, as described by Treadwell ("Kurzes Lehrbuch der Analytischen Chemie," vol. ii., p. 184). The results were low, 0.004733 to 0.004776 grm. molybdenum per c.c. Converting the molybdenum trisulphide to molybdenum disulphide, as used by Blair ("Chemical Analysis of Iron," 4th Edition, pp. 199–200), was attempted, with no uniform results. Evaporating the molybdate solution with dilute nitric acid in a platinum dish was then tried, adding more nitric acid, and evaporating to dryness several times, to obtain molybdenum trioxide. This gave high results, 0.005064 to 0.005095 grm. per c.c.

As these high results might be due to small traces of alkali in the ammonium molybdate, or other impurities, it was thought that the best method to separate them would be to use the electrolytic method, as given by Kollock and Smith (Journ. Am. Chem. Soc., 1901, xxiii., 669). Accordingly, different amounts of the molybdate solution were electrolysed according to their conditions of precipitation, using a platinum dish as a cathode. After the deposition was complete (on testing the solution by adding hydrochloric acid, tin, and potassium thiocyanate, no red colour was obtained), the sesquioxide was dissolved in nitric acid, evaporated to dryness, and heated to constant weight. The results checked those of the lead molybdate precipitation, i.e., 0.004908 grm. per c.c.

Having determined the strength of the molybdate solution, the potassium permanganate solution was standardised against it, under the following conditions:—Volume, 200 c.c.; acidity, 6 c.c. of concentrated sulphuric acid; temperature, 21° C. A reductor 45 c.m. long and 1.5 c.m. in diameter was used, filled with granulated zinc. The solution was poured into the reductor, and then suction applied. The solution was run through the reductor twice, followed by 200 c.c. of water, not allowing air to be sucked through during the pouring, and titrated immediately with potassium permanganate. A "blank" consisting of 200 c.c. of water and 6 c.c. concentrated sulphuric acid was run, and the permanganate required was subtracted.

Separation of Molybdenum from Iron by Precipitation as Molybdenum Trisulphide by Hydrogen Sulphide under Pressure and Titration with Potassium Permanganate.—Different proportions of molybdenum and iron were taken and treated in the following manner:—The molybdate and iron solutions were run into a pressure bottle (as previously described), and a drop or two of dilute sulphuric acid added to prevent the formation of a precipitate of ferric molybdate. Two hundred c.c. of sulphuric acid (1:20) were then saturated with hydrogen sulphide, and added to the pressure bottle, at the room temperature. Then a very rapid stream of hydrogen sulphide was passed through the solution in the bottle, which prevented the sulphide from adhering to the glass tube. The bottle was closed and placed in a boiling water-bath, and heated for from one to

two hours, then allowed to cool, emptied into a beaker, the bottle washed out with water, and the precipitate allowed to settle. The solution was filtered through a Gooch crucible by decantation, using suction, and washed with about 300 c.c. of dilute sulphuric acid (1:50) saturated with hydrogen sulphide. The precipitate was transferred to the Gooch crucible, and washed two or three times with water. The precipitate and filter were transferred to a casserole, 10 c.c. concentrated sulphuric acid, 10 c.c. concentrated hydrochloric acid, and 5 c.c. concentrated nitric acid were added, and the contents evaporated to fumes of sulphur trioxide. Dissolving the precipitate directly through the filter by different acids was tried, but without success. In evaporating to fumes of sulphur trioxide, great trouble was experienced at first by the bumping of the solution. This was finally overcome by blowing air through the solution during the evaporation. After evaporation, the solution was allowed to cool, diluted with water, and washed into a beaker. A slight excess of ammonia was added, and the solution filtered to remove the asbestos and a small quantity of ferric hydroxide. The precipitate was washed with hot water until the filtrate had a volume of 200 c.c., neutralised with sulphuric acid, 6 c.c. concentrated sulphuric acid added, and allowed to cool. When at room temperature, the solution was reduced and titrated under exactly the same conditions as used in standardising. The results obtained are given below:—

Iron taken. Gm.	Molybdenum taken. Gm.	Molybdenum found. Gm.
0.10760	0.00197	0.00189
0.10760	0.00197	0.00220
0.10760	0.00492	0.00487
0.10760	0.00984	0.01163
0.10760	0.02460	0.02374
0.10760	0.04921	0.04953
0.05380	0.04921	0.04937
0.02690	0.04921	0.05095
0.00538	0.04921	0.04875
0.00215	0.04921	0.04969

In each case it was observed that there was iron present after dissolving the molybdenum trisulphide in the mixture of acids, and adding ammonium hydroxide. Therefore, it was thought advisable to determine whether the iron was carried down with the molybdenum sulphide, either mechanically or chemically, or whether it came from some outside source.

Two solutions containing 0.1076 gm. iron and 0.04921 gm. molybdenum were precipitated with hydrogen sulphide under pressure, and treated as already described. Having dissolved the molybdenum trisulphide, ammonia was added to the solution in excess, and the solution filtered. The precipitate remaining on the filter had the characteristics of ferric hydroxide, and, when dissolved in hydrochloric acid, gave a deep red colour with potassium thiocyanate. A blank consisting of asbestos, water, and the same amounts of acids was run under the same conditions, and gave only a trace of iron. This showed that the iron present came from the precipitation with hydrogen sulphide under pressure, and proved that it is necessary to remove it by adding ammonium hydroxide. In order to determine whether it was possible to obtain any precipitation of iron by hydrogen sulphide under pressure, two similar solutions were precipitated under the same conditions, except that no molybdenum was added, and no iron was found. In order to determine the amounts of iron present, several tests were made upon varying proportions of molybdenum and iron. The operation was conducted according to previous conditions, and the iron weighed as ferric oxide in a platinum crucible.

Molybdenum taken. Gm.	Iron taken. Gm.	Ferric oxide obtained. Gm.	Iron obtained. Gm.
0.00492	0.10760	0.00010	0.00007
0.00984	0.10760	0.00020	0.00014
0.02460	0.10760	0.00030	0.00021
0.04921	0.10760	0.00050	0.00035

Each ignited precipitate was red, and when dissolved in hydrochloric acid gave a deep red colour with potassium thiocyanate. These results indicate that the contamination is mechanical.

Separation of Iron from Molybdenum by Precipitating the Iron as Ferric Hydroxide by Sodium Hydroxide and Titrating the Molybdenum with Potassium Permanganate.—As there seemed to be some difference of opinion in regard to the use of sodium hydroxide or ammonium hydroxide in precipitating iron from a molybdate solution, it was thought advisable to determine which precipitant gives the best results. (Cf. F. T. Kopp, *Journ. Am. Chem. Soc.*, 1902, xxiv., 186; J. Brakes, *Journ. Soc. Chem. Ind.*, 1902, xxi., 832; G. Auchy, *Journ. Am. Chem. Soc.*, 1902, xxiv., 273, and 1903, xxv., 215).

Varying proportions of molybdenum and iron were taken and precipitated by adding 70 c.c. of sodium hydroxide solution (1:10) to the mixture of molybdenum and iron in a bulk of 50 to 60 c.c. acid with 2 c.c. sulphuric acid. The solution was stirred, the precipitate allowed to settle, and then filtered and washed with hot water until the filtrate had a volume of 200 c.c. The precipitates of ferric hydroxide were dissolved in dilute sulphuric acid, and reprecipitated and washed as before. The filtrates obtained were neutralised with sulphuric acid, then 6 c.c. concentrated sulphuric acid added to each, allowed to cool, reduced, and titrated as usual.

Iron taken. Gm.	Potassium permanganate required for first filtrate. C.c.	Potassium permanganate required for second filtrate. C.c.	Molybdenum found. Gm.	Molybdenum taken. Gm.
0.00215	16.15	0.05	0.05041	0.04921
0.00538	16.2	0.00	0.05041	0.04921
0.02690	16.2	0.05	0.05057	0.04921
0.05380	16.2	0.05	0.05057	0.04921
0.10760	16.1	2.00	0.05072	0.04921
0.10760	7.9	0.00	0.02458	0.02460
0.10760	3.3	0.00	0.01027	0.00984
0.10760	1.7	0.00	0.00529	0.00492
0.10760	0.75	0.00	0.00233	0.00197

All but one of the results are slightly high. In order to determine whether this might be overcome by increasing the strength of the sodium hydroxide solution used for precipitation, 0.04921 gm. of molybdenum and 0.1076 gm. of iron were precipitated in 50 c.c. bulk with 70 c.c. of sodium hydroxide solution (1:5). The amount of molybdenum found in the two filtrates was 0.05088 gm. Then 0.04921 gm. molybdenum and 0.1076 gm. iron were taken and precipitated as before, using 105 to 110 c.c. sodium hydroxide solution (1:5). The amount of molybdenum found was 0.05057 gm. This showed that the discrepancy cannot be eliminated by the addition of more of the precipitant. In order to find out whether these high results were due to impurities in the iron solution used, 0.1076 gm. of iron was taken and 2 c.c. sulphuric acid added as before, and precipitated in 50 c.c. bulk with an excess of sodium hydroxide, and treated as before. The number of c.c. of potassium permanganate required was the same as for the blank.

Separation of Iron from Molybdenum by Ammonium Hydroxide, without Boiling out the Excess of Ammonium Hydroxide, and Titration with Potassium Permanganate.—This series of experiments was carried out under the same conditions as when precipitating with sodium hydroxide, 30 c.c. ammonium hydroxide (sp. gr. 0.9) being added in excess.

Iron taken. Gm.	Potassium permanganate required for first filtrate. C.c.	Potassium permanganate required for second filtrate. C.c.	Molybdenum found. Gm.	Molybdenum taken. Gm.
0.00215	16.5	0.00	0.05134	0.04921
0.00538	16.65	0.00	0.05184	0.04921
0.02690	16.75	0.00	0.05212	0.04921
0.05380	15.9	0.5	0.05103	0.04921
0.10760	16.3	0.4	0.05197	0.04921

These results show conclusively that sodium hydroxide gives a more accurate separation of iron from molybdenum than ammonium hydroxide.

In order to determine whether the excess of ammonium hydroxide caused this increased discrepancy, ammonia was added as before, and then boiled out completely with the following results, the other conditions being maintained as given:—

Iron taken.	Potassium permanganate required for first filtrate.	Potassium permanganate required for second filtrate.	Molybdenum found.	Molybdenum taken.
Grm.	C.c.	C.c.	(rm)	Grm.
0.00215	16.1	0.05	0.05010	0.04921
0.00538	15.2	0.35	0.04839	0.04921
0.02690	15.15	0.5	0.04870	0.04921
0.05380	13.15	1.35	0.04512	0.04921
0.10760	11.20	0.8	0.03734	0.04921
0.10760	1.80	2.25	0.01260	0.02460
0.10760	0.35	0.2	0.00171	0.00984
0.10760	0.3	0.00	0.00093	0.00492
0.10760	0.05	0.00	0.00015	0.00197

These results show that boiling the ammonia out of the solution renders the results worthless. As the molybdenum solution, when treated alone, gave no precipitate, the error is due to the formation of an iron molybdate which is precipitated in a neutral solution.

This fact led to the belief that the high results obtained in the sodium hydroxide and ammonium hydroxide separations were due to the formation of a ferric molybdate, which was slightly soluble in excess of sodium or ammonium hydroxide, and thus caused high results by the iron being reduced and titrated together with the molybdenum.

Ibbotson and Brearley ("Analysis of Steel-works Materials," p. 81) state that when an alkali is added to an acidified mixture of ferric chloride and molybdic acid, a point is reached at which an insoluble basic ferric molybdate is formed, and no perfect separation of the two metals is possible until sufficient alkali has been added to decompose this compound. Also that similar bodies are formed during the separation of chromic, tungstic, or vanadic acid from iron.

It was then undertaken to find iron in the filtrate after separation of the iron by the ammonium hydroxide. Two portions containing 0.04921 grm. of molybdate and 0.1076 grm. of iron each were taken, and precipitated by ammonia, as described. The solutions were filtered, washed with water, and the filtrates (200 c.c.) were neutralised with sulphuric acid, and to c.c. of concentrated sulphuric acid added in excess. Then the molybdenum was precipitated from this solution by hydrogen sulphide under pressure. The solutions were allowed to cool, and filtered. The filtrates were evaporated to small bulk, ammonia added, and the solution filtered. The precipitates were washed and dissolved in hydrochloric acid. The filtrate from one was divided into two equal portions:—To one-half, potassium thiocyanate was added, and a red colour obtained; the other half was re-precipitated with ammonia, and re-dissolved in hydrochloric acid, potassium thiocyanate added, and a red colour obtained. The filtrate from the other was precipitated twice with ammonia, and finally dissolved in hydrochloric acid, potassium thiocyanate added, and a deep red colour obtained. The precipitate of ferric hydroxide was plainly visible. A blank consisting of 200 c.c. of water and 10 c.c. of sulphuric acid was run under the same conditions, and only a trace of colour was obtained, and no precipitate of ferric hydroxide could be seen. The precipitates of molybdenum trisulphide were dissolved in nitric, hydrochloric, and sulphuric acids, and evaporated to fumes of sulphur trioxide. The solution was allowed to cool, diluted a little, ammonia added, and filtered. The precipitates were dissolved in hydrochloric acid, and potassium thiocyanate added, and red colours were obtained. The experiment was repeated using 0.24605 grm. of molybdenum and 0.538 grm. of iron. In

precipitating with hydrogen sulphide, the hydrogen sulphide gas was passed through two plugs of asbestos, and through two wash-bottles, in order to prevent any iron from being carried over from the generating flask. The iron was precipitated twice with ammonia, ignited, and weighed as ferric oxide. The weight of ferric oxide found was 0.0005 grm. This was dissolved in hydrochloric acid, potassium thiocyanate added, and a deep red colour obtained.

These experiments show that the high results obtained are due to the formation of a ferric molybdate in small amount, which is soluble in the excess of the precipitant.

The reason that we can find the iron by the foregoing method is probably because the relative concentration of molybdenum and iron is changed, and therefore not as much ferric molybdate is formed as in the initial precipitation, thus allowing some of the iron to be precipitated by ammonium hydroxide.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 12, September 19, 1904.

Chemical Composition of Adrenaline.—Gabriel Bertrand.—The author describes a method of purifying adrenaline. He proves that the substance can be obtained pure by making two series of fractional precipitations and analysing the final fractions separately. The four analyses quoted have concordant results, and give $C_9H_{13}NO_3$ as the empirical formula. This formula was formerly proposed by Aldrich. The molecular weight (174.3, instead of 183) obtained by cryoscopic methods corresponds to the same formula.

Nomenclature of the Rosanilines.—Jules Schmidlen. The author criticises the nomenclature recently proposed by M. Baeyer as leading to very complicated terms, e.g., chloride of diaminomethylfuchsonimine for rosaniline chlorhydrate. He suggests instead a modification of the old nomenclature which retains many of the ancient terms and yet is quite exact. His system is shown in the following table:—

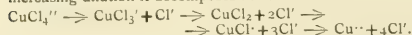
Ancient names.	Modifications.
Pararosaniline	Rosaniline.
Rosaniline	Rosamonotoluidine.
Fuchsin, C_{21}	Rosaditoluidine.
New fuchsin	Rosatritoluidine.
Aniline blue	Triphenylosaniline.
Crystalline violet ..	Hexaphenylosaniline.

Tetraoxycyclohexane Rosanilines. New List of Colourless Derivatives.—Jules Schmidlen.—The nomenclature in this paper is that described in the preceding abstract. In a former paper the author described the formation of tetrachlor- and tetraminocyclohexane rosaniline, the colourless addition products of rosaniline salts. He now finds that the salts of rosadi- and rosatritoluidine can take up four molecules of water when dissolved in concentrated HCl and allowed to stand. It is known that, in the case of salts forming addition products with an acid, a base, or a neutral body, their state of non-saturation is due to the presence of a non-saturated carbon atom, which can take up monovalent groups. Hence there must be present four carbon atoms with double linkings in the molecule of rosaniline salts.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxvii., No. 13, 1904.

Fluorescence. The Ring System of Benzene.—Hugo Kauffmann.—The author examined the effect of Tesla currents upon substances belonging to various classes, e.g., carbohydrates, phenol ethers, amines, &c., using either alcohol or acetic acid as solvent, and found that violet fluorescing substances yield vapours which become luminous under the influence of Tesla currents, and the colour of the luminescence agrees with that of the fluorescence. From this experimental result it follows that the ring in violet fluorescing benzene derivatives is in the same condition as in those substances which give a violet fluorescence under the influence of Tesla currents (X or D condition). Two points are to be taken into consideration in studying all luminescence caused by radiant energy—absorption and emission. Thus, from experimental results we see that the emission is the same in fluorescence and in luminescence caused by Tesla currents, and that in both cases it depends upon the condition of the benzene ring. This is not the case with the absorption. In the Tesla experiments the reason for the absorption lies in the benzene ring itself, but in fluorescence, which is caused by absorption of ultra-violet light, some other reason must be sought. Certain groups must be present in order that a substance may fluoresce, e.g., the carbethoxyl group. Thus the aniline ring gives no fluorescence though it luminesces, whereas anthranilic acid ester both luminesces and fluoresces. In investigating the phenomenon of fluorescence absorption and emission must be examined as separate phenomena. By studying the fluorescence of dihydrocollidine dicarbonic acid diethyl ester it may be proved that the violet emission is connected with the existence in the ring of parallel double bonds.

Metallic Nitroso Compounds.—V. Kohlschütter and M. Kutscheroff. —*Cupric Nitroso Compounds.*—On electrolysing concentrated solutions of copper chloride part of the copper migrates from the cathode. The quantity of copper which is transferred to the anode rapidly decreases with dilution, and the negative transport numbers soon assume their normal values. This phenomenon is to be ascribed to the formation of the cupric salt of a cupric-hydrochloric acid with the anion, CuCl_4'' . This anion is only stable in presence of excess of chlor ions, and with increasing dilution it decomposes as follows:—



In studying the formation of cupric nitroso compounds the authors found that in aqueous solution the quantity of NO absorbed by copper chloride is never very large, and rapidly diminishes with dilution. Absorption only takes place within the limits of concentration in which the transport numbers were found to be abnormal, i.e., in green solutions, and ceased entirely as soon as the dissociation became normal. Hence the power of cupric chloride solution of absorbing NO is connected with the formation of complex ions. Since addition of chlorides increases the absorption in solutions containing the same quantity of copper chloride, it is clear that it is specially the anions containing copper which take up the nitric oxide, for an excess of chlor ions favours the formation of the complex anions. The examination of the phenomenon of the absorption of nitric oxide by copper chloride dissolved in various other solvents all goes to show that the absorption always depends upon anions containing copper and never upon the copper cations. The solutions which absorb NO are never blue, but always green or brown. These latter contain complex anions, or cations, to which negative residues are still attached. All solutions give up their NO on standing in the air or on dilution with water. Solid copper salts do not absorb the gas.

Rapid Method of Distinguishing Rosaniline and Pararosaniline.—Rudolf Lambrecht and Hugo Weil.—Commercial rosaniline dissolves completely on warming in 20 parts by volume of 30 per cent hydrochloric acid. No

crystals separate out from the solution even on standing for some days, while pararosaniline on addition of the same quantity of hydrochloric acid forms the difficultly soluble chlorhydrate which crystallises out on cooling. If only $\frac{1}{2}$ per cent of pararosaniline is present in commercial rosaniline, after twelve hours brown crystals appear, while larger quantities, amounting to 5 to 10 per cent, give crystals immediately on cooling. The brown pararosaniline chlorhydrate thus separated becomes dark green after standing for six weeks over caustic lime, and then contains 3 molecules of hydrochloric acid besides water of crystallisation. It is noteworthy that commercial rosaniline on solution in less than 20 parts of hydrochloric acid after standing gives crystals of polychlorhydrate.

A New Molybdenum Carbide, MoC.—H. Moissan and M. K. Hoffmann.—A mixture of 25 grms. of coarsely powdered molybdenum and 25 grms. of aluminium in small pieces with 0.2 gm. of petroleum coke was heated in a charcoal crucible in an electric oven for not more than three minutes, a current of 500 amperes and 100 volts being employed. The crucible must be quite closed with a layer of charcoal. On cooling and breaking up the molten metallic mass, crystals of a dark colour were seen embedded in yellow laminated aluminium carbide. The metal was coarsely powdered and treated in the cold with a mixture of concentrated caustic soda and potash, when a gas was energetically evolved. The metal was then digested with caustic alkali for three or four days on the water-bath, the alkali being renewed from time to time till no more hydrogen was evolved. A black crystalline powder then remained, which was heated on the water-bath for twenty hours with dilute sulphuric acid (3 parts concentrated acid to 1 part water), washed with cold concentrated hydrochloric acid, and finally with water, and dried at 100°. Thus a mixture of graphite and a grey crystalline, much heavier, powder was obtained, and the latter was separated from the graphite first by means of a sieve and then by the addition of bromoform. The molybdenum carbide, MoC, thus obtained is a grey powder which is seen under the microscope to consist of prismatic glittering crystals. Its density is 8.40 at 20°. It easily scratches glass and quartz but not ruby. It is not attacked at a red heat by pure dry hydrogen nor by steam at 600°. It burns in fluorine, forming CF_4 and a white molybdenum fluoride. At a red heat chlorine converts it into molybdenum chloride and amorphous carbon. Heated in presence of air or oxygen it forms molybdenum trioxide and carbon dioxide. It is scarcely attacked by boiling aqueous hydrochloric acid, reacts very slowly with concentrated hydrofluoric acid, and is decomposed by boiling concentrated sulphuric acid and by nitric acid in the cold.

Phosphorescing Substances.—K. A. Hofmann and W. Duca.—The authors found that among 15 preparations of blende made from perfectly pure zinc ammonium sulphate not one phosphoresced, even intense Becquerel rays only causing feeble luminescence. But commercial zinc chloride, treated strictly according to Henry's directions, gave visible luminescence on exposure to daylight or Becquerel rays. The qualitative analysis of the zinc chloride used showed the presence of the following impurities:—Small quantities of lead, nickel, iron, calcium, and silicon, and relatively large amounts of potassium, sodium, and magnesium, and the addition of these substances to pure zinc ammonium sulphate gave luminescing blends. For a blende of very strong yellowish green luminescence the authors added 100 c.c. of 8 per cent aqueous ammonia to a solution (slightly acidified with sulphuric acid) of 20 grms. of the purest zinc ammonium sulphate, 5 grms. of sodium chloride, and 0.2 to 0.5 gm. of crystallised magnesium chloride in 400 c.c. of distilled water and allowed to stand for twenty-four hours; the clear filtrate was saturated with sulphuretted hydrogen, the sulphide collected and dried at 100° without previous washing. It was then powdered, and ignited in a covered porcelain crucible for thirty minutes in a larger vessel placed in a Perrot or

Rössler gas-oven. This crystalline pale yellow preparation is very strongly affected by Becquerel rays, cathode rays, arc light, or daylight. Sunlight through blue, violet, or green glass acts very strongly, while yellow or red light completely stops the phosphorescence. The blende thus prepared luminesces under the influence of a strongly active substance. If pure magnesium sulphate and pure potassium chloride are used instead of magnesium chloride and sodium chloride the same effect is obtained, but neither pure alkali chloride nor pure magnesium salt alone is sufficient. Possibly by admixture of alkali chloride the crystallisation of the sulphide at white heat is expedited, for which reason repeated heating with an equal weight of sodium chloride has a favourable effect upon the power of becoming luminescent. The addition of magnesium salts removes impurities, such as arsenious acid or antimony oxide, from the ammoniacal solution, but the authors could not get phosphorescing preparations from the purest zinc ammonium sulphate, which contained no trace of arsenic or antimony, or any impurity, without the help of magnesium or alkali salt. Hence the luminous effect must be due to the magnesium directly, or to an admixture contained in the magnesium salt. If the latter were the case, the filtrate from the ammoniacal mixture precipitated with sulphuretted hydrogen should be free from, or at any rate poorer in, the active mixture, as this would be precipitated with the zinc sulphide. But with such a filtrate, using the purest zinc ammonium sulphate and ammonia as described above, the authors obtained a preparation as active as before. Hence, they assume that the magnesium salt remaining in the zinc sulphide on filtration as well as the alkali chloride is necessary for the preparation of the strongly phosphorescing blendes. The presence of some metals (one part per thousand), e.g., iron, nickel, cobalt, bismuth, chromium, copper, reduces the luminescence, while others, e.g., zinc, selenium, manganese, and cadmium, have the opposite effect. The phosphorescing blendes show no trace of radio-activity.

MISCELLANEOUS.

St. Louis Exhibition Awards.—Messrs. A. Boake, Roberts, and Co., Ltd., Stratford, have received a cable from the St. Louis Exhibition intimating that they have been awarded Grand Prize, 2 Gold Medals, and a Silver Medal. Their exhibit was composed of Chemicals (principally sulphites and phosphates), Materials for Brewing, and Essences for aerated waters and confectionery purposes.

NOTES AND QUERIES.

Plastic Materials.—In an article by S. S. Sadtler (CHEMICAL NEWS, vol. xc., p. 184 *et seq.*) I find several recipes for plastic materials. Would any of those recipes be of use to make underground pipes? Would the recipe for powdered anthracite coal and molasses require much pressure, and what would be a suitable binder to use? I want, if possible, to get a material that can be moulded without pressure.—HILLIARD STEPHENS.

MEETINGS FOR THE WEEK.

FRIDAY, 28th.—Physical, 5. "An Interference Apparatus for the Calibration of Extensometers," by John Morrow and E. L. Watkin. "A Sensitive Hygrometer," by Dr. W. M. Thornton. "Note on a Property of Lenses," by Dr. G. E. Allan.

UNIVERSITY OF BIRMINGHAM.

ASSISTANT LECTURER AND DEMONSTRATOR IN
CHEMISTRY.

The Council invites applications for this Appointment.

The stipend will be £150 per annum. The Candidate selected will be required to enter on his duties at the earliest possible date. Further particulars may be obtained from the undersigned, to whom applications, accompanied by testimonials, should be sent not later than November 7th, 1904.

GEO. H. MORLEY, Secretary.

UNIVERSITY OF GLASGOW.

ADDITIONAL EXAMINERSHIPS.

The University Court of the University of

Glasgow will shortly proceed to appoint the following additional Examiners:—

(a) For Degrees in Arts and Science.—One Examiner in MATHEMATICS. Annual salary, £70.

(b) For Degrees in Arts, Science, and Medicine.—One Examiner in NATURAL PHILOSOPHY (including PRACTICAL PHYSICS). Annual salary, £70. Candidates should be qualified both on the Mathematical and Experimental side.

One Examiner in CHEMISTRY. Annual salary, £50.

The appointments will be for three or four years from January 1st, 1905, and, in addition to the above-mentioned salaries, hotel and travelling expenses will be paid.

Candidates should lodge twenty copies of their application and testimonials with the undersigned on or before NOVEMBER 12th, 1904.

ALAN E. CLAPPERTON,
Secretary, Glasgow University Court.

97, West Regent St.,
Glasgow.

BIRKBECK COLLEGE,

Breams Buildings, Chancery Lane, E.C.

DAY AND EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHAN, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board,
Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.



Glew's Scintilloscope.

Brilliant Scintillations from PITCHBLLENDE, Ra, Po, U, Th, or any source of Alpha-Rays.

A Welsbach mantle excites the extremely sensitive transparent screen of the Scintilloscope.

Scintilloscope, complete, with 2 sensitive screens, charged with Polonium and Pitchblende respectively, in pocket case 7/6 post free

Pieces of Pitchblende, ground flat, with sensitive screen attached, showing scintillations with any strong pocket magnifier, from 7/6 each, post free.

Radium, &c, for
Lectures on hire.

F. H. GLEW,
156, Clapham Road, London, S.W.

MELTING & BOILING-POINT TABLES.

BY
THOMAS CARNELLEY,

D.Sc. (Lond.), B.Sc. (Vict.), F.C.S.,

Professor of Chemistry in University College, Dundee.

The Standard and only work upon the subject.

2 Vols. Ry. 4to. 799 pp. 42s.

HARRISON & SONS, Pall Mall, London, S.W.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC,

As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET
LEAD and PIPE, LITHARGE, SHOT, &c.

SECOND EDITION, NOW READY.*With Illustrations.*

Price 2s. net (post free 2s. 1½d.)

Mme. CURIE'S Thesis

ON

RADIO-ACTIVE SUBSTANCES.REPRINTED from the **CHEMICAL NEWS.****CONTENTS.**

Introduction.—Historical.—Chap. I. Radio-activity of Uranium and Thorium; Radio-active Minerals.—Chap. II. Method of Research.—Chap. III. Radiation of the New Radio-active Substances.—Chap. IV. Communication of Radio-activity to Substances Initially Inactive.—Nature and Cause of the Phenomena of Radio-activity.

r6, NEWCASTLE ST., FARRINGDON ST., E.C.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

r6, NEWCASTLE ST., FARRINGDON ST., E.C.

E. GEORGE & SONS,
BOOKSELLERS.

161, WHITECHAPEL ROAD, LONDON, E.

Are OPEN to PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application.

BRYAN CORCORAN LIM.MILLSTONE BUILDERS,
WIRE WEAVERS. MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.Sole Makers of MILBURN'S
Patent Conoidal Stone Grinding Mills.
Especially suitable for certain materials, Wet or Dry.Works and Warehouses: Back Church Lane.
Payroll Dept.: Basement of the Corn Exchange.

31, MARK LANE, LONDON.

**MICA** Telephone
No. 2248 Avenue.**F. WIGGINS & SONS,** 10, Tower Hill, E., &
103 & 103, Minories, E.C., London.
MICA MERCHANTS.Manufacturers of Mica Goods or Electrical and ALL purposes.
Contractors to His Majesty's Government.**SILICATES OF SODA AND POTASH.**IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.
FULL STRENGTH GUARANTEED.**OLDEST AND MOST RELIABLE MAKE.***Supplied on best terms by***WILLIAM GOSSAGE & SONS, Ltd.,** Soap Works, Widnes
LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.**RADIUM BROM.**

Of 2,000,000 unit strength.

TWO TUBES of 5 Milligrams. each
and ONE TUBE of 2½ Milligrams.
At £5 per mg. for cash.

Also a few Typical Specimens of the following:—

ÆSCHYNITE**SAMARSKITE**

Containing—	Per cent.	Containing—	Per cent.
Niobium oxide ..	22	Niobium oxide ..	56
Titanium ..	29	Iron oxide ..	13
Thorium ..	15·7	Uranium oxide ..	14 to 20
Cerium ..	18·4	Yttrium ..	8 to 11
Lanthanum ..	2·6	Thorium ..	6
Didymium ..	2·6	Zirconium ..	4
Yttrium ..	1·1	And traces of Cerium, Calcium, &c.	

(URAL MOUNTAIN).

(URAL MOUNTAIN).

MONAZITE**LITHION GLIMMER**

Phosphoric acid..	28	Lithium oxide ..	2 to 5
Cerium oxide ..	37 to 45·7	Fluoric acid..	4 to 8
Lanthanum oxide ..	27·4	Rubidium, Cæsium, Thallium, &c.	
Thorium oxide ..	18	(SAXONY).	
Traces of Calcium, Magnesium, Tin.			

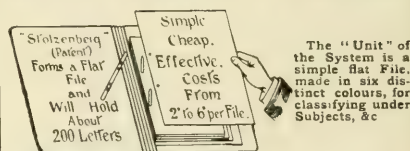
(NORWAY).

At 3/6 to 4/- each.**ARMBRECHT, NELSON & CO.**

71 & 73, Duke St., Grosvenor Square, W.

Perfect Order amongst your
Scientific Papers,
Research Records, &c.,

IS SECURED BY THE

**“STOLZENBERG”
SYSTEM OF FILING.**

The “Unit” of the System is a simple Flat File, made in six distinct colours, for classifying under Subjects, &c

Used by SIR WILLIAM CROOKES, LORD KELVIN, Royal Commission on Tuberculosis, Baden Alkali Works (50,000), and by thousands of private persons as well as Business Concerns.

Satisfaction guaranteed; otherwise goods taken back and money returned.

Sample Set, consisting of 12 best Files, 4to and fcap., with strong nickel-plated Perforator, and Patent Lifter, packed in leather-board box, 10/6 post free.

THE STOLZENBERG PATENT FILE CO.,
50, Bishopsgate St. Without, London, E.C.

THE CHEMICAL NEWS.

VOL. XC., No. 2344.

NOTES ON THE FRACTURE OF STRUCTURAL STEEL UNDER ALTERNATING STRESSES.*

By JOHN OLIVER ARNOLD,
Professor of Metallurgy, Sheffield University College.

THE efforts of steel metallurgists and engineers to obtain scientific control over the mechanical properties of steel used for structural engineering purposes, although attended with much success, have nevertheless presented certain unfortunate features of failure. Thirty or forty years ago, it was claimed, apparently with reason, that if the chemical constituents of mild steels were identical, their mechanical properties were necessarily similar. But as experience extended, it soon became evident that steels registering practically the same chemical analyses gave astoundingly different mechanical tests. The next stage of research led to the enunciation of the generally accepted idea that steels having a good chemical composition correlated with satisfactory tensile and bending tests, were thoroughly reliable. But the advent of high speeds placed engine parts under rapidly alternating tensile and compression stresses, the reversals being in some instances at the rate of 800 per minute. Under these new conditions the sense of security ensured by a good chemical composition and satisfactory static tests, was rudely disturbed by the fact that steel in a relatively small number of cases was liable to fracture far below its elastic limit, more after the manner of glass than of a ductile metal.

These facts led to a remarkable development of the micrographic method of examining steel. The results obtained have thrown considerable light upon the matter, but after fifteen years' correlative research the inexorable logic of facts compels the author to state with regret that in connection with this particular matter the microscope in its turn has, to a considerable extent, broken down in its attempt to solve that mystery of steel, of all others the most important practically, namely, the cause and prevention of its sudden rupture under vibration and alternation, two phenomena probably closely allied. The author here wishes to emphasise and reiterate the fact that he is discussing steels possessing great toughness and ductility under ordinary static tests.

To pass from generalities. The author, through the kindness of his friend, Mr. J. T. Milton, Chief Engineer of Lloyds, is enabled to publish, with a certain degree of reserve, important facts ascertained during a two years' research carried out with the assistance of his friend and colleague, Mr. Andrew McWilliam, A.R.S.M., at the University College of Sheffield, under instruction from Lloyds' Committee.

To select one instance. The shell plates of the boiler of a Colonial cruiser, split longitudinally from end to end, under the hydraulic test. The fractured plates were about 1 inch thick, and each weighed nearly three tons. The average analysis of the plates was about as follows:—

Carbon		0.20
Silicon		0.02
Manganese		0.50
Phosphorus		0.04
Sulphur		0.04
Copper		
Arsenic		Very low

Of course the above analysis is beyond reproach. Pieces from the fractured plate, bent double, and closed right up

* Read before the British Association (Section G), Cambridge Meeting, 1904.

under violent hammering, without any sign of flaws. The average tensile tests registered about:—

Elastic limit		15 tons per square inch
Maximum stress		29 tons per square inch
Elongation		29 per cent on 2 inches
Reduction of area		50 per cent

The above mechanical tests leave little to be desired. The microscopical structure showed a distinct and unusually sharp segregation of the pearlite and ferrite, the latter being angular and intensely crystallised. It was also large in pattern, and frequently occurred in those long white lines, rich in sulphur and phosphorus, which are technically known as "Ghosts."

In the early stages of the research it was thought that the sharp crystallisation might be regarded as an effect due to that cause which produced also the effect of brittleness. As will be seen presently, this theory was decisively negated by subsequent experiments. In order to measure the mechanical brittleness incapable of being detected by ordinary static or bending tests, the author caused to be devised a machine in which the test piece is placed under rapid and severe alternating stresses slightly beyond its elastic limit, the amount of strain being necessarily relatively small. The number of alternations are registered by a counter, adjusted to zero for each test. The rate of alternation can be varied at will, and in the near future these data will be supplemented by a record of the energy expended per test piece, ascertained by means of a delicate integrating Watt meter.

This method of testing (which practically carries out the almost impracticable Wöhler test in one or two minutes) has already thrown important light on the obscure phenomena under investigation, and has also exhibited remarkable delicacy. These facts are proved by the data now submitted to the section by the author.

In preliminary tests on standard English acid open hearth boiler plate steel the remarkable fact was noted that in all probability the resistance of structural steel to rupture under rapidly alternating stresses is inversely proportional to the rate of alternation. This law, if fully established by the exhaustive experiments now being carried out at the Sheffield College, demands careful attention from every engine designer. The following figures indicate concretely the data upon which the author provisionally enunciates the law. The subjoined table has reference to alternating shock bending tests carried out on a good boiler plate steel, the test bars being $\frac{3}{4}$ inch square, and the bending force being applied $\frac{1}{4}$ inches from the line of maximum stress, with a range of $\frac{1}{16}$ inch each side.

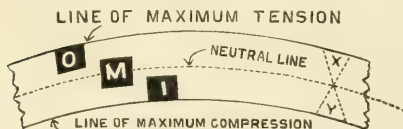
Mark	Rate of alternation.	Number of alternations necessary to complete fracture.
S 1	168 per minute	1330
S 2	" "	1456
S 3	" "	1352
S 4	" "	1361
Mean		1375
S 5	266 per minute	860
S 6	" "	870
S 7	" "	916
S 8	" "	868
Mean		878

Whilst the above results exhibit considerable concordance, those obtained from the fractured boiler plate were so erratic that for a time the author was almost in despair—when the curious clue to the situation presented itself, that one side of the plate was brittle, and the other tough under alternating stresses. This theory, about to be put to a most careful experimental test, but in the meantime the following data are, in all probability, substantially accurate:—

Mark.	Rate of alternation per minute.	Number of alternations endured.	Heat treatment.	Probable position of test-piece.
L 3	168	420	Heated to 950° C. and cooled in air.	Inside
L 4	168	1232		Outside
L 7	168	1378	Oil quenched from 950° C.	Outside
L 8	168	694		Inside
L 11	266	433	As received.	Inside
L 12	266	864		Outside
L 18	266	260	Heated to 950° C. and cooled in air.	Inside
L 19	266	500		Outside
L 20	266	388	Annealed, heated to 950° C., slowly cooled.	Inside
L 21	266	781		Outside
L 22	266	630	Oil quenched from 950° C.	Outside
L 23	266	240		Inside
L 26	266	400	Water quenched from 900° C.	Doubtful
L 27	266	336		Doubtful

The somewhat disconcerting lessons to be drawn from the above table are:—1. That once a steel has assumed decisive brittleness in alternation, it cannot be restored by heat treatment of any kind, short of re-melting. 2. That the injury to this steel was on one side of the plate, and hence due to unskilful re-heating of the ingot, and not to an improper casting temperature, since the latter must necessarily have affected every portion of the plate. A third and still more regrettable confession has also to be made, namely, that the microstructures of the pairs, including both brittle and tough steel, were in all respects identical, though, of course, that of each pair varied with the heat treatment to which they had been subjected.

The author wishes, finally, to record some delicate and interesting tests obtained from an inch plate of mild steel bent over a radius considerably shorter than that of a large boiler, namely, about 2 feet. In such a plate the inside radius will represent a line of maximum compression stress, the outside radius a line of maximum tensile stress, and a radius exactly between the two will touch a neutral line. (See accompanying figure).



If from the apices of two V's, x y, progressing inwards and outwards, lines are drawn to the inner and outer circumferences, these V figures will qualitatively represent the increasing intensity of the stresses at increasing distances from the neutral line. As to the quantitative value of these angles, the author has no practical data. The following table records the influence of stress in deteriorating the metal next the inner and outer radii, and also that immediately adjacent to the neutral line.

Mark and position.	Rate of alternation per minute.	Number of alternations endured.	Remarks.
O	266	916	Mean of ten tests.
I	266	996	" "
M	266	1067	" "

It will be seen that, in its resistance to fracture under alternating stresses, the portion of the plate in tension is inferior to that in compression; whilst the steel about the neutral line is superior to that next the inner radius.

All the results recorded in this paper are preliminary, having been carried out on an extemporised machine. A standard machine has now been erected at the Sheffield College, from which the author hopes to obtain in the near future standard data as to the influence of sizes and shapes of test pieces, length of stroke, rate of alternation, and the correlation (if any) between these data and the energy necessary to produce fracture.

PRESENT PROBLEMS OF ORGANIC CHEMISTRY.*

By W. A. NOYES.

THERE is a strong tendency on the part of some chemists, at the present time, to claim that chemical science in the true sense includes only such portions of our knowledge as can be stated in accurate mathematical terms. One distinguished representative of this school of chemistry has said, "It is not in the province of science to explain phenomena," and another has written, "It is not a part of its ultimate object (*i.e.*, of natural science) to acquire knowledge in regard to mentally conceived existences, such as the atoms of matter, or the particles of luminiferous ether, which are of such a magnitude and character as to lie far beyond the limits of human perception." I think that nearly all of those now actively engaged in working over the problems of organic chemistry would dissent strongly from these statements. Long experience in dealing with the cumulative, non-mathematical evidence upon which our knowledge of chemical structure is founded has led to a very firm conviction that human knowledge is not bounded by the limits of sense-perception. We are inclined rather to the view that, while there are, undoubtedly, many things which will always remain beyond any direct cognisance of our senses, yet, so far as these have a real existence, we may in the end secure, regarding them, very practical and positive knowledge. It is impossible to conceive that those theories with regard to structure which have guided the work of thousands of chemists for the last fifty years do not in some measure express the actual truth with regard to atoms and their relation to each other in organic compounds.

Let us follow, for a few moments, in very brief outline, the steps which have led to the present standpoint. So far as the matters which interest us most are concerned, there was practically no knowledge of organic chemistry before the nineteenth century. The first steps were, of course, the preparation of pure substances and the development of accurate methods of analysis. In both of these fields Liebig was the great master. The formulae which were calculated were at first of little value except to check the accuracy of the analyses and as a simple expression for empirical composition. I need not dwell on the confusion which existed throughout the first half of the century because there was no agreement as to the basis for molecular weights or atomic weights, nor upon the large part played by the study of organic compounds in finally clarifying the view of chemists upon these matters. Yet, in spite of this confusion, two discoveries of fundamental importance date from this period:—(1) That the empirical composition alone does not fix the nature of a compound, *i.e.*, the fact of isomerism; (2) that certain groups of atoms may remain together in passing from one compound to another through a whole series. The first fact furnishes one of the strongest reasons why an empirical formula for an organic compound is not enough, and the second fact furnishes the most important experimental basis at the foundation of our structural formulae.

The studies of this period furnished a knowledge of the empirical composition of many natural products and of the products obtained from these by oxidation, reduction, and the action of various agents. But while some might, perhaps, be inclined to look upon this mass of empirical knowledge as the most valuable acquisition of that time, and to think that the theories in vogue were so imperfect or erroneous as to be of no value, such a view is certainly superficial. There were plenty of chemists in that day, too, who were ready to decry theories which seemed to them worthless, and it is interesting to read to-day what the great Laurent said upon this matter. He wrote in 1837 (*Liebig's Ann. de Chem.*, xxii., 143):—"If I could believe that the purpose of my work was only to find a few new compounds, or that it would end in my being able to

* Read at the International Congress of Arts and Science in St. Louis, September 21, 1904. From *Science*.

say that there is an atom more or less in this compound or that, I would give it up on the spot. Only the desire of finding an explanation for some phenomena and of proposing some more or less general theories can give me the courage to follow a course in which I have found so little encouragement and where I have met with so many obstacles to overcome." Any one who has followed the story of how the older theories of radicals paved the way for the theory of types, and of how the typical formulae were so easily transformed into structural formulae when the fact of valence was once grasped, cannot fail to see that the larger and fuller view is an outgrowth from the earlier theories. And we must acknowledge that Laurent was right, and that the theories upon which he was working were of vastly more importance than the mass of empirical facts which furnished him with their scaffolding.

Do not misunderstand me. There were two theories of radicals at that time—one which devised radicals in the study which should accord with the electro-chemical theories held at the time, and which did not attempt to secure evidence of their existence from the conduct of the compounds containing them, another which kept in much closer touch with the facts discovered in the laboratory. It was only the latter theory which contributed much to the growth of our knowledge. A theory which cannot secure for itself a sound experimental basis is, of course, of only ephemeral value.

These, then, are the steps which have led to our present standpoint in organic chemistry:—The discovery of isomerism, the discovery of radicals, the older radical theory, the theory of types, the establishment of true molecular weights, the discovery of the fact of valence, the determination of structure.

I think that all workers in organic chemistry will accept the following as a conservative statement of our present knowledge:—(1) That in organic compounds, at least, each atom is attached *directly* to only a limited, small number of other atoms; (2) that in the sense of the order of the successive direct attachments, the structure of a very large number of compounds is known with a degree of probability that amounts to practical certainty.

This brings me to the task which has been set, an attempt to outline the problems which lie before us in the further development of our science.

In the first place there is still much to be done to extend our knowledge of compounds found in nature. This field is much less cultivated, relatively, than was the case sixty years ago. There has been good reason for this because of the problems of absorbing interest which have arisen in the preparation and study of new compounds, and in the extension of our knowledge of old ones. But there must still remain many compounds to discover, both among animal and vegetable products. On this side organic chemistry resembles the descriptive sciences of botany, zoology, and mineralogy. And just as botanists think it worth their while to secure as complete a description as possible of the plants to be found on the earth, so it lies in our province to isolate and identify the carbon compounds of the animal and vegetable worlds—with the difference that in our case each compound, new or old, may be the starting-point for the preparation of an almost endless number of others. But here most of us recognise that unless a compound has some further interest than that it is new it is not worth the time taken in its preparation. I am afraid, however, as we look over the pages of our journals there is too much evidence that not every one lives up to this view. Our ever-increasing army of nascent doctors must needs have something to do, and it is so easy to make new compounds and so difficult to find something new of larger scope and really worth the doing.

There still remains much to do in the determination of the structure of compounds which have long been known. The study of a single compound often involves an incredible amount of work. Baeyer worked with indigo for fifteen years before his labours were crowned with a successful synthesis, and twenty years more and the work

of very many chemists were needed before the scientific achievement could become a commercial success.

It was nearly twenty-five years after the first structural formula was proposed for camphor before Bredt was fortunate enough to suggest the true arrangement of its atoms, and it was ten years longer, and required in all the work of more than fifty chemists, before Bredt's suggestion was confirmed by Komppa's beautiful synthesis.

More than thirty formulae were proposed for camphor, and those who think little of organic chemistry have some reason if they say that we jump at conclusions too hastily and propose too many formulae that are mere guesses. Some might even say that the last formula is not worth much, but those who have followed the matter know that step by step we have arrived at an almost positive certainty even in this complex problem.

The final solution of a problem with regard to the structure of a compound of natural origin is not usually considered to have been satisfactorily attained until its synthesis has been effected. Those who have attempted work of this character know that months or even years of work are frequently spent to obtain the synthesis of a single compound. In spite of the wealth of methods at our command—a wealth so great that it is often very difficult to select between several which are equally unpromising—it is evident that these methods of synthesis need improvement at many points. Not only do we need new and better methods, but many old methods require further study to disclose why they succeed in some cases and fail in others, and to secure a fuller knowledge of secondary reactions which often occur. As recent remarkable achievements in this field of synthetic methods may be mentioned the brilliant results obtained by Grignard with magnesium compounds, Bouveault's elegant new solution of the old problem of transforming an acid into the corresponding alcohol, and Scheuble's reduction of the amides of bibasic acids to the corresponding glycols.

Work along the lines suggested needs to be done in order to fill out and complete our knowledge in a systematic way, and occasionally work along such lines is rewarded by results of epoch-making significance, as when Gomberg discovered triphenylmethyl in his endeavour to prepare hexaphenylethane. Such work is not likely, however, to greatly advance our insight into the real nature of carbon compounds, and we all feel that there are far more fundamental problems which demand attention.

As outlined above, the theories of valence and of structure now universally accepted imply a certain amount of knowledge of the arrangement of atoms in space. So far as the original and fundamental conceptions are concerned, however, this knowledge is quite vague. The much more definite conception proposed by van't Hoff, and in a somewhat different manner by Le Bel, is of course familiar to you all. In discussing any hypothesis it is always important to have clearly before us the facts upon which it is based. As I have already hinted, I believe that the theory of valence and the theory of structure, in the sense of a sequence of atoms within the molecule, are supported by our knowledge of such a vast accumulation of consistently interrelated phenomena that we are justified in believing that we have positive knowledge with regard to the structure of the molecules of organic compounds. I am as ready as any one to demand that every theory, no matter how old or how universally accepted, shall be continually brought back to the test of agreement with experimental facts, but I am not willing to admit that we may not, in the end, acquire positive knowledge by the process of inductive reasoning.

Assuming, then, the fact of a knowledge of the sequence of atoms in organic compounds, we have this basis for van't Hoff's hypothesis:—1. When four unlike atoms or groups are combined with a single carbon atom, optical activity results in such a manner that there may always be found two compounds having identical sequence of the atoms within the molecule, and exactly equal rotary power but of opposite signs. 2. That when two adjacent carbon atoms are combined, each with three unlike groups, two

compounds may result which, while optically inactive and having the same sequence of atoms, still differ in physical properties. An illustration of this is found in racemic and mesotartaric acids. 3. Rings containing five and six atoms are formed with especial ease, those containing three, four, and seven atoms less readily, and rings containing more than seven atoms are scarcely known. 4. Derivatives of cyclopropane, cyclobutane, cyclopentane, and cyclohexane, having two substituents combined with different carbon atoms, often exist in two isomeric forms in which the sequence of the atoms is the same. 5. Derivatives of ethylene often exhibit a similar isomerism.

Assuming as true that we have acquired a knowledge of the sequence of atoms in carbon compounds, the facts which I have enumerated lead almost inevitably to the corollary that the four atoms attached to a given carbon atom are arranged in approximate symmetry around the centre of that atom for their position of most stable equilibrium. The relation between this conclusion and the theory of the sequence of atoms in carbon compounds, or what is ordinarily understood as structure, is very similar to the relation between the atomic theory and Avogadro's law. If we accept the atomic theory, there seems to be no rational escape from the acceptance of Avogadro's law. In a similar manner, if we accept the theory of the sequence of atoms in carbon compounds, there seems no reasonable possibility other than that van't Hoff's hypothesis is true in its broad outlines.

I hope I may be pardoned here for a brief digression. I am aware that Franz Wald (*Zeit. Phys. Chem.*, 1897, xxiv., 633) believes that he can give a satisfactory explanation of the laws of fixed and multiple proportion, and of combining weights without the aid of the atomic theory, and that Professor Ostwald, in his recent Faraday lecture, has accepted and expanded the same thought (*Journ. Chem. Soc.*, xxv., 506). I will say frankly that their reasoning does not appear to me conclusive. Ostwald defines a chemical individual as "a body which can form hylotropic phases within a finite range of temperature and pressure" (*Journ. Chem. Soc.*, xxv., 515), and deduces from this the fact that a given hylotropic phase must have a fixed composition. He appears to forget that the existence of these hylotropic phases implies that the properties of matter are discontinuous, or, in other words, that there is a finite number of hylotropic bodies, one of the facts for which the atomic theory gives an explanation.

There is another characteristic, too, of a chemical compound which all chemists will agree is at least as important as that it shall consist of a "hylotropic phase." This is that the compound must not only have a fixed composition, but this composition must bear a definite relation to those numerical quantities which represent the proportion in which each element of which it is composed always combines with other elements. I need hardly add that these numerical quantities are so deeply seated in the properties of matter that, having adopted a unit, all chemists are absolutely agreed in selecting one, and only one, such quantity for each of the well known elements.

In attempting to deduce this law of combining weights Ostwald assumes that three elements form the compounds AB, AC, BC, and ABC, and adds:—"There shall be but one compound of every [each] kind." With this assumption, his reasoning may be sound, but I fail to see how it applies when we find ten thousand compounds ABC instead of one. The case which he supposes is so far theoretical that I have been unable to find an actual case where the compound ABC can be formed, both by the union of AB with C, and of AC with B.

(It is quite possible that such an illustration may be found, but, in any case, Professor Ostwald's deduction can not be made to apply to those cases in which the compound ABC does not exist, nor to those cases where the compound ABC cannot, even theoretically, be supposed to consist in turn of a known compound AB combined with C, and of another known compound AC combined with B. Such cases are common because of the fact of valence. In

its simplest form the law of combining weights is quite independent of the existence of the compound ABC, and may be stated thus:—"If the composition of two compounds AB and BC has been determined, the composition of a series of compounds between A and C can be predicted, and a compound which does not belong to this series has never been discovered." A still more general statement of the law, and one which includes, by implication, all of those facts which are used in the selection of atomic weights, is given above. In that form it is more properly called the law of atomic weights).

But I have taken too much time with a matter which is aside from my main purpose. Before leaving this topic I must add, however, that I have used the phrase "Avogadro's law" advisedly in spite of the fashion set by some chemists of calling it Avogadro's hypothesis.

(Two reasons may be given for this usage. My own view is that we have, by a process of inductive reasoning, acquired much positive knowledge of the existence of atoms and molecules that the expression "Avogadro's Law" is fully justified. But even if we admit the contention of those who think that the atomic theory must always remain an unproved hypothesis, it is possible to frame a definition of the word molecule which would be merely a generalised statement of those empirical facts which lie at the basis of our atomic and molecular theories. Such a generalised empirical definition must, of course, be very complex, but it would not include the concept of discrete particles. Yet it will be still true of these empirically defined molecules that equal volume of gases contain equal numbers under the same conditions of temperature and pressure. For instance, the term gram-molecule may be considered as a purely empirical generalisation, and it is true that a gram-molecule of one gas occupies the same volume as a gram-molecule of any other other. But this is, in essence, Avogadro's Law).

I remarked a few moments ago that the facts which have been outlined almost compel us to the acceptance of van't Hoff's hypothesis in some form. It is of the utmost importance for us to recognise, however, that we are here at the very confines of our present knowledge, and that we must, at every step, bring ourselves back to the rigorous test of experimental fact. In accepting the hypothesis we are not compelled to consider molecules as set pieces of mechanism; on the contrary, there is strong reason for thinking that the positions assumed by the atoms are positions of dynamic and not of static equilibrium. While there have been many speculations in the matter, we have no strong reason for assuming, as yet, any definite shape for the carbon atom, nor even that there are within it definite points of attraction for other atoms. All that seems to be thoroughly established is that for their position of most stable equilibrium, the four atoms or groups attached to a given carbon atom are arranged in approximate symmetry around its centre. I say *approximate* symmetry, because the existence of compounds containing rings of three and four carbon atoms demonstrates that the symmetry is not always absolute, and makes it probable that in cases where the four atoms or groups are unlike the symmetry is also imperfect. So far as I am aware no fact inconsistent with this fundamental conception is known, while very many facts about optically active and cyclic compounds find in this conception the only satisfactory explanation which has thus far been given. It is true also that many facts with regard to optically active compounds indicate that when one group is exchanged for another the exact configuration is often retained, or, in other words, the entering group takes the same position with regard to the other three atoms or groups as was held by the group which was displaced. The manner in which it has been possible to work out consistently the complex relations between a considerable number of sugars, gives a very strong experimental basis for this statement. On the other hand, it is well known that such reactions often give racemic mixtures, which indicates that a shifting of groups with regard to a central carbon atom takes place much

more easily than the shifting of a group from one carbon atom to another, at least in saturated compounds. There are also a number of extremely interesting cases where a reaction gives rise to the optical antipode. Thus Walden has shown that *l*-chlorosuccinic acid is converted by silver oxide into *l*-malic acid, while potassium hydroxide converts it into the dextrorotatory acid (*Ber.*, 1899, xxii., 1855). It is evident that in one case or the other there has been a shifting of the groups. Again, Ascham has shown that when *d*-camphoric acid is heated with hydrochloric and acetic acids it may be about half converted into *l*-isocamphoric acid, and that the latter suffers a similar transformation (*Ber.*, xvii., 2004). This case is more complicated, as a "cis" and "trans" isomerism of cyclic compounds is involved, as well as the optical difference. Not many cases of this character are known at present, but such cases certainly deserve further study, and must be reckoned with in considering the question we have before us. Le Bel (*Journ. Chim. Phys.*, 1904, ii., 344) has already pointed out the theoretical significance of Waldron's work.

While we may feel that we have comparatively sure ground in the application of the theory of van't Hoff and Le Bel to optically active and to cyclic compounds, the case is quite different when we come to the consideration of what are commonly known as "double" and "triple" unions. Professor Michael has done a very great service to chemistry in showing that the supposition of a more or less definite tetrahedral shape for the carbon atom and of "favoured" configurations often lead to conclusions which are at variance with the facts. Philips (*Am. Chem. Journ.*, xxiv., 428) and Blanchard (*Ibid.*, xxvi., 281; xxvii., 428) and myself have found a case in which the addition of hydrobromic acid to an unsaturated compound produces an optically active body, which evidently has the same configuration as the amino and hydroxy acids from which the unsaturated body is formed by the loss of ammonia or of water. We have here, apparently, a potential asymmetry occasioned by the double union which it is difficult to reconcile with the prevailing conception of such unions. This case is complicated by the presence of a second asymmetric carbon atom in the molecule and is worthy of further study. Rabe and Billmann have recently described a similar case, but very few instances of this kind are known (*Liebigs Ann. d. Chem.*, cccxxiii., 25).

Pfeiffer (*Zeit. Phys. Chem.*, xliii., 40) has recently suggested a new interpretation of van't Hoff's hypothesis as applied to unsaturated compounds. Pfeiffer assumes that unsaturated compounds retain essentially the same configuration as the saturated compounds from which they are derived. On this side his interpretation is closely related to the old theory of free valences, which, if I understand him correctly, is favoured by Professor Michael. Pfeiffer also brings his interpretation into a close relationship to Werner's theory of inorganic metallic compounds. The most serious objection to the theory is that it supposes the existence either of trivalent carbon atoms or of free valences, in ethylene and its derivatives, an objection which has appeared to most chemists very strong in the past. Pfeiffer points out, it is true, that since the discovery of triphenylmethyl we can no longer deny the possible existence of a trivalent carbon atom.

(The fact that triphenylmethyl exists as a doubled molecule in solution should not, I think, lead us to discard the monomolecular formula for a very many more than we consider that acetic acid has, in the ordinary sense of structure, a doubled molecule, because it exists as a doubled molecule in solution in benzene, or in the state of vapour just above its boiling point, nor because it forms acid salts. In these cases the chemical evidence appears to be more important and more conclusive than the physical. It is probable that the doubled physical molecule is the result of forces which do not produce a stable structure in the ordinary sense.)

It would seem, however, that the great difference between the intense chemical activity of triphenylmethyl and the comparative inactivity of ethylene demonstrates that, if the latter does in reality have free valences, the fact that

there are two such valences reduces the activity of each enormously. The inactivity of carbon monoxide may be significant in this connection.

A more serious objection to Pfeiffer's hypothesis lies in the fact that he supposes so slight a difference in the configuration of fumaric and of racemic acids, that it is difficult to see why the former as well as the latter might not be split into a pair of optically active bodies.

(To be continued.)

THE USE OF COMPLEX SALTS IN ELECTROLYTIC ANALYSIS. SEPARATIONS OF COPPER FROM ARSENIC AND ANTIMONY, OF NICKEL FROM ZINC, OF ZINC FROM IRON, &c.

By A. HOLLARD and L. BERTIAUX.

WHEN from a mixture of several metals in saline solution we wish to separate one only of them by means of the electric current, it suffices, when possible, to change the other metals, which should remain in the bath, into the state of complex salts. These metals, which are then no longer in the state of ions, but are contained in the complex ions, can no longer be deposited under the influence of the current. If, for example, we require to change arsenic and iron into the state of complex salts we can form the following compounds:—

$\text{Na}_3(\text{AsO}_4)$, dissociable into the ions $3\text{Na} + \text{AsO}_4$;
Arseniate of sodium.

$\text{K}_4(\text{Cy}_6\text{Fe})$, dissociable into the ions $4\text{K} + \text{Cy}_6\text{Fe}$.
Ferrocyanide of potassium.

The arsenic and the iron in this state cannot be deposited on the cathode; at the most they might be deposited on the

anode in the form of the complex ions AsO_4 and Cy_6Fe .

The use of complex salts for electrolytic separations was recommended some years ago by Freudenberg (*Zeit. Phys. Chem.*, vol. xiii., p. 97), but the method has been very little used, no doubt on account of the difficulty experienced in a mixture of salts, of making some only of them go into the state of complex salts.

We will now describe the manner in which we have used complex salts in electrolytic analysis:—

1. Copper is frequently accompanied by notable quantities of arsenic, both in its ores and in raw copper. The electrolytic estimation of the copper is then rendered impossible, because the arsenic is deposited with the latter portions of the copper; the copper becomes black, and if the amount of arsenic present is in any way large the deposit is spongy, and does not adhere to the cathode. We have succeeded in preventing the deposition of the arsenic on the cathode by making it pass into the form of

the ion AsO_4 , and keeping it in this state. When we electrolyse a nitric solution of copper and arsenic, the

arsenic certainly goes into the state of AsO_4 ions, but under the reducing influence of the current it soon passes into the state of As ions, and is deposited on the cathode.

To maintain the arsenic in the state of AsO_4 ions, it suffices to add ferric sulphate to the bath (a quantity corresponding to 0.1 grm. is quite enough), the copper is then deposited in the pure state. When the copper is accompanied by antimony, we add SO_4Pb before the electrolysis (0.4 grm. is quite sufficient); the peroxide of lead which is then deposited on the anode retains the antimony (see Hollard, *Bull. Soc. Chim.*, 1903, vol. xxix., p. 155).

2. Separation of Nickel from Zinc.—We have already shown that the electrolytic separation of nickel and zinc is

impossible by the ordinary methods of electrolysis on account of the very close values of their tensions of polarisation. Nevertheless, we have already pointed out a means of effecting this separation; it consists in preventing the disengagement of oxygen at the anode by making use of a soluble anode (Hollard, *Bull. Soc. Chim.*, 1903, vol. xxix., p. 116), or by the addition of a suitable reducing agent (Hollard and Bertiaux, *Bull. Soc. Chim.*, 1904, vol. xxxi., p. 102); the resistance of the bath is then sufficiently reduced for the separation to take place. We will now describe a new method for this separation. It consists in changing the zinc to the state of a complex nitrite of zinc and ammonium. We have made quite certain that this salt does not give any deposit of zinc by

electrolysis; thus there are no Zn^{++} ions formed in solution; this is, consequently, a complex salt to which we can give the provisional formula $2NO_2Am_4(NO_2)_2Zn = Am_2[(NO_2)_4Zn]$, a complex nitrite of zinc and ammonium, dissociable into ions of $2Am$ and $(NO_2)_4Zn$. The method of operating is as follows:—

The nickel and zinc in the form of sulphates are treated successively with 5 grms. of sulphate of magnesia, 25 c.c. of ammonia at $22^\circ B$, dilute sulphuric acid until the bath is slightly acid, 12.5 grms. of nitrate of ammonia, and, finally, with at least 25 c.c. of a saturated solution of sulphurous acid. Boil until the odour of sulphurous acid has disappeared, dilute with water, and add 25 c.c. of ammonia at $22^\circ B$.

The solution, diluted to 300 c.c., is submitted to a current of 1 ampère at a temperature of about 85° . The electrodes have been described already (Hollard, *Bull. Soc. Chim.*, 1903, vol. xxix., p. 1074). The nickel is deposited in a few hours at the most.

Results of Experiments.

Amount taken.		Ni deposited.
Zn.	Ni.	
0.2552	0.2500	0.2547
0.2552	1.0000	0.2530
0.2552	0.0000	0.2536
0.2552	0.2500	0.2544
0.2552	1.0000	0.2547

3. We have found another manner of applying complex salts to the separation of zinc and iron by changing the latter to the form of ferrocyanide. The solution of the metals in the form of sulphates is treated with a large excess of a saturated solution of SO_2 , and then heated; this reduces the iron. When the solution is decolourised the heating is still continued to drive off the excess of SO_2 . Add carbonate of soda to the very hot solution until an abundant precipitate is formed, then a solution of sulphurous acid until the latter is re-dissolved; finally a mixture of 30 c.c. of cyanide of potassium at 20 per cent, and 50 c.c. of soda at $15^\circ B$. In this manner the iron passes into the state of ferrocyanide. Dilute to 300 c.c., and electrolyse in the cold with a current of 0.4 ampère, with a cathode previously covered with copper. The zinc deposited may contain 1 or 2 milligrms. of iron (see below) which can be estimated by means of permanganate of potash. The presence of aluminium does not interfere provided there is not more than 0.5 gm. present.

Results of Experiments.

Amount taken.			Zn deposited.	Iron.
Zn.	Fe.	Al.		
Grm.	Grm.	Grm.	Grm.	Grm.
0.2500	0.1000	—	0.2516	0.0011
0.2500	0.2000	—	0.2517	0.0010
0.2500	0.1000	—	0.2514	0.0026
0.2500	0.2000	—	0.2513	0.0014
0.2500	0.2000	0.5000	0.2541	0.0016
0.2500	0.2000	0.5000	0.2531	0.0011

4. We have also used complex salts for the separation of tin and antimony from copper. We have already described this method, in the year 1900, in a paper on the "Analysis of Commercial Copper" (Hollard, *Ann. de Chim. Analytique*, p. 330). We referred to it again in 1903 (Hollard, *Bull. Soc. Chim.*, vol. xxix., p. 262). Our reason for mentioning these dates is that this process has been published under the name of Mr. Arthur Fischer in the *Berichte* (No. 36, July 11, 1903, pp. 2348—2356), and we claim priority.

Classen has shown that antimony and tin in solution in concentrated sulphhydrate of sodium ($d = 1.22$) could be separated easily by the electric current; the antimony alone is deposited on the cathode. The tin remains behind in the bath in a state of complex combination. With this method of Classen's the increasing amount of polysulphides which is formed round the anode during the course of the electrolysis may pass by diffusion as far as the cathode, where it is able to dissolve the deposited antimony. To prevent the formation of polysulphides, Mr. Fischer proposes adding cyanide of potassium to the bath. Now we have used this reagent long before he did and at the dates we have given above. Further, we have shown that cyanide of potassium has the great advantage of preventing the copper, which almost always accompanies antimony, from being deposited with it during the electrolysis. In fact, the copper alone passes into the state of a complex salt. It may appear strange for the copper to accompany the antimony in a solution of hydrosulphate of sodium in which the copper is supposed to be insoluble. But actually, its solubility is very noticeable in concentrated hydrosulphate of sodium ($d = 1.22$), as we have already shown (Hollard, *Comptes Rendus*, 1896, vol. ccxiii., p. 1063; *Ann. de Chimie Analytique*, 1897, p. 242).

According to the formulæ we have given of the complex ions, it would seem that the metal of the complex ion is never able to be deposited on the cathode. However, it can be so deposited in the case of a certain number of complex salts; the potassic cyanides of silver, gold, mercury, and cadmium, for example. This takes place because certain complex ions are themselves partly dissociated. In such a case the metal present in the complex anion may be deposited directly on the cathode as with a simple salt. As a matter of fact, the concentration of the ions of the metal of the complex salt is always very slight, and we know that, according to Nernst's formula,—

$$e = \frac{K}{v} \log \frac{P}{C}$$

that the tension of polarisation e of a salt is inversely to the concentration C of the ions of the metal.

Nevertheless, the complex salts may be of great service in electrolytic analysis, because even when they are dissociated the metal can only be deposited under the influence of a tension of polarisation much higher than the tension of polarisation of the simple salt.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 15.

RADIUM RAYS AND BENZENE DERIVATIVES.

By HUGO KAUFFMANN.

In order to examine thoroughly into the phenomenon of fluorescence the relations between emission and chemical constitution must be understood. The power of emission will be found to be the same in very many substances, whether they fluoresce or not. In the case of fluorescence other definite conditions also exist, as, for example, the power of absorption for ultra-violet rays.

The radium rays seem to me to afford a very suitable form of energy to apply in the study of the power of emission of various substances. This idea of mine has actually been confirmed. By far the greater number of benzene derivatives are excited to luminescence by the radium rays, many of them so strongly that the luminescence is visible,

even at a distance of 10 c.m. from the radium preparation. After the rays have penetrated a sheet of metal. The experiments were so arranged that the substance to be examined was placed on a sheet of copper about 0.07 m.m. thick, and by means of a special appliance this sheet was placed at certain measurable distances over the radium. Five m.grms. of very active radium bromide were used, contained in a rubber capsule.

The organic compounds examined were used in the solid crystalline state.* Very small quantities of impurities seem to produce a great effect. Thus, for example, of two specimens of hydroquinone di-methyl ether, one of which was quite pure, and the other only slightly adulterated, only the former showed strong power of luminescence. After the second specimen had been distilled no difference could be detected between the two.

The benzene derivatives having many rings show the greatest power of luminescence, and specially those whose vapours give a violet luminescence under the influence of the Tesla currents, i.e., those whose benzene rings are in the X or D condition. Such compounds as appear luminescent at a distance of 12 c.m. from the radium to an eye thoroughly accustomed to the darkness I call very strongly luminous under the influence of the radium rays. Such compounds are, for example, phenanthrene, retene, anthracene, β - β -dinaphthylamine, di-tolylimide, di-phenyl-indol, β , β -dimethoxystilbene. The following luminesces more feebly (in some cases much more feebly):—Phenyl- β -naphthylamine, α - and β -naphthylamine, carbazole, β -anisidine, β -dinaphthyl ether, acenaphthene, naphthalene.

Benzene derivatives whose vapours do not luminesce in the Tesla experiments are in some cases excited very strongly by the radium rays, and in many cases not at all. β -Dibromobenzene and m -dinitrobenzene luminesce only at a distance of some millimetres from the radium. Azobenzene shows no effect in an experiment arranged as above.

Coloured benzene derivatives are apparently very little affected by radium rays, e.g., azobenzene, the nitranilines, diphenylamine quinoxaline, and α -amino-cinnamic acid. These two last compounds are specially noteworthy, for they fluoresce, and it might be supposed that fluorescence is directly connected with susceptibility to the influence of radium rays. But this is not the case, or at any rate there is no direct connection, for these two last compounds only luminesce at a distance of about 2.1 c.m.

The parallelism between the luminescence excited by Tesla currents and that caused by radium rays is obviously fairly far-reaching. If it were thoroughly established we could base upon it a simple convenient method of determining and measuring the X or D condition of the ring system of a solid benzene derivative.

By studying dihydrocollidine-dicarboxylic acid diethyl ester we are enabled to form a tolerably definite opinion as to what part of the benzene ring is responsible for the observed emission. This compound possesses an enormous power of luminescence, far exceeding that of any organic compound yet investigated, and in this respect may be compared with the platinum cyanides. At a distance of 2.5 c.m. it is excited to distinct luminescence by radium rays, which had passed through a zinc plate of 0.75 m.m. thickness. At shorter distances an effect is perceptible, even if the rays have penetrated a layer of three or four such zinc plates.

Screens which are made with this ester can be used for investigating radio-active phenomena almost as well as those of barium platinum cyanide. They have the advantage of being cheaper. (They are, however, not quite so active).

The dihydrocollidine-dicarboxylic acid diethyl ester is just as sensitive as the above dihydrocollidine compound. As these two compounds have only the two parallel double bonds of the six-ring in common with the benzene derivatives in the X condition, which are also excited by radium

rays, it is highly probable that in the case of the substances examined in general the emission of light is conditioned by the presence of these double bonds.

The colour of the emitted light is scarcely recognisable in the case of most substances; in very luminescent colourless substances it is blue to violet; dihydrocollidine dicarboxylic acid diethyl ester gives a very beautiful blue luminescence.

I have also performed experiments to determine which of the radium rays cause the luminescence. It appears that the spots of light projected on substances by radium rays are very easily deflected by an electro-magnet, and thus the β -rays produce the principal effect. Similarly, the Röntgen rays, which closely resemble the γ -rays, frequently had an effect, but always to a slight extent. In the case of these substances which are only capable of being excited at a distance of a few millimetres, the α - and not the β -rays possibly play the principal part.—*Berichte*, 1904, xxxvii., 2946.

RADIO-ACTIVE CINNABARYTES.

By S. M. LOSANITSCH

I HAVE recently examined, for radio-activity, various Serbian ores and other minerals, and have found that native cinnabarytes from two different places (Avala and Bare) has a decided radio-active effect upon the photographic plate. I propose to give here the results of these experiments, with some deductions from them. After I had proved the activity of these Serbian mercury ores, I examined foreign ones also, but then I found that only the ores from Idria (Austria), and especially the variety known as "Ziegeleerz" (brick-ore), are radio-active. Further investigations will perhaps show that many other mercury ores are accompanied by a radio-active element.

To detect the radio-activity, dry silver bromide gelatin plates were used. The powdered specimens contained in a lead vessel with a paper bottom were placed on the plates and left there for three to four days. The plates, when developed and fixed, showed almost equally strong reactions with all these specimens; these reactions were, however, decidedly feebler than those of pitchblende.

The first indications of radio-activity I detected in a cinnabarytes from Avala. But this ore is often permeated with metallic mercury; hence, I considered it necessary to convince myself whether in this experiment the reduction of the photographic plate was not caused by the mercury vapour. Two experiments were sufficient to decide this question; viz., first I showed that pure cinnabarytes crystals are radio-active, and then I convinced myself that metallic mercury under similar circumstances caused no reduction of the photographic plate. Thus the active effect of cinnabarytes is to be ascribed to a radio-active element.

The mercury ores from Avala are often so intimately mixed with barytes that there is no doubt that they have originated contemporaneously. Hence, I thought at first that the barium, as the compound homologous to radium, was the carrier of the radio-activity. But I soon found that the particles of barytes picked out of the mineral are not in the least radio-active. This result led me to the conclusion that the radio-active constituent of cinnabarytes cannot be radium. For if radium were the active constituent of cinnabarytes from Avala, then we could not explain why two elements so closely related as barium and radium, minerals of which have originated contemporaneously in Avala, should have separated from one another from a mixture of the two when the rock was formed. If we further reflect that the radio-active constituent of this cinnabarytes occurs with many other cinnabarytes, then we are led to the assumption that probably the radio-active element of cinnabarytes is allied to mercury, and that therefore it must belong to the Zn—Cd—Hg series of the Periodic System of the elements,

* As far as the experiments show at present no luminescence appears when the substances are in solution.

It may perhaps be a radio-mercury, if I may be allowed to give it a name.

The radio-active constituent of cinnabarites has given equally strong reactions in the case of all specimens examined, which reactions, as I have mentioned before, are much weaker than those of pitchblende. The feeble effect of this radio-active constituent may perhaps be due to the smallness of the amount present. But in my opinion this weak reaction is also a proof that radio-mercury is not identical with radium, but that it is a less strongly active element which belongs to a later less positive homologous series of the Periodic System. As I shall explain later in a theoretical treatise, all these homologous series end with a radio-active element. Moreover, the radio-active elements in the different homologous series differ from one another in the strength of their radiation, according as they belong to the more or less positive homologous series. It is very probable that the radio-active elements in strongly positive homologous series emit stronger radiations than those radio-active elements which belong to the less positive series. According to this supposition it is clear why radium, which belongs to the second strongly positive homologous series, should emit stronger radiation than radio-mercury, which belongs to the ninth, only feebly positive homologous series.

Volatility is known to be a characteristic property of the Zn-Hg series, and thus radio-mercury, if it is a homologue of these elements, ought also to be volatile. This agrees with the fact that the residual portion of roasted cinnabarites shows no radio-activity. Thus roasting the ore has caused the radio-mercury to volatilise with the mercury, which would not be the case if it were identical with radium.

Summary.—By photographic experiments I have shown that certain mercury ores are radio-active, and I have expressed the opinion, based upon certain suppositions, that the radio-active constituent of the mercury ore is a radio-mercury. I hope to confirm this opinion by experiments which I propose to perform very shortly.—*Berichte*, 1904, xxxvii., 2904.

THE DETERMINATION OF MOLYBDENUM IN STEEL AND IN STEEL-MAKING ALLOYS.*

By FREDERICK VAN DYKE CRUSER

and
EDMUND H. MILLER.

(Concluded from p. 207).

PART I. (continued).

Separation of Iron from Molybdenum by Sodium Hydroxide and Precipitation of the Molybdenum as Lead Molybdate. (Brearley, *CHEMICAL NEWS*, 1898, lxxviii., 203; Abs., *Journ. Chem. Soc.*, 1899, lxxvi., 129. Chatard, *CHEMICAL NEWS*, xiv., 175. Brearley, *CHEMICAL NEWS*, 1899, lxxix., 2, and 14; Abs., *Journ. Chem. Soc.*, 1899, lxxvi., 336. Ibbotson and Brearley, *CHEMICAL NEWS*, lxxix., 3; lxxxi., 269).—In order to test the accuracy of the lead molybdate precipitation compared with the titration by potassium permanganate, a series of experiments were undertaken, using the same concentrations of molybdenum and iron as before. The details are as follows:—Two c.c. of hydrochloric acid (sulphuric acid could not be used on account of the subsequent precipitation by lead acetate) were added to each solution, and they were then diluted to from 50 to 60 c.c., 70 c.c. of sodium hydroxide (1:10) were added, and the solution filtered and washed until the filtrate was about 150 c.c. in volume. The precipitate of ferric hydroxide was re-dissolved by hydrochloric acid and re-precipitated as above. The filtrates were combined and boiled down to 200 c.c. An excess of ammonium hydroxide

was added, then 2 to 3 c.c. excess of acetic acid (33 per cent), and 5 to 6 grms. of ammonium chloride. The solution was heated to boiling, 20 to 50 c.c. lead acetate solution (40 grms. per litre of lead acetate) added, depending on the amount of molybdenum present, and the solution stirred vigorously for from two to four minutes, and then treated as under the conditions already given for standardising the molybdate solution.

In measuring the small amounts of molybdenum for the test, 5 c.c. of the standard molybdate solution were diluted to 100 c.c. and the proportional amount used.

Iron taken.	Molybdenum taken.	Lead molybdate found.	Molybdenum found.
Grm.	Grm.	Grm.	Grm.
0.00215	0.04921	0.1920	0.05022
0.00538	0.04921	0.1915	0.05010
0.02690	0.04921	0.1932	0.05054
0.05380	0.04921	0.1927	0.05040
0.10760	0.04921	0.1900	0.04994
0.10760	0.02460	0.0958	0.02306
0.10760	0.00964	0.0403	0.01054
0.10760	0.00492	0.0204	0.00534
0.10760	0.00197	0.0084	0.00220

From these results we see that the estimation of molybdenum, after the separation of the iron as ferric hydroxide, by titration and by precipitation with lead acetate is about equally accurate. The molybdate precipitation has a slight advantage in accuracy, but as it takes very much longer, the titration method is to be preferred. Two of the precipitates of lead molybdate were dissolved in concentrated hydrochloric acid, diluted with an equal volume of water, and extracted with 50 c.c. of ether; the ether solution drawn off, diluted with water, the ether evaporated off, hydrochloric acid, and then ammonium hydroxide added. The solution was filtered, and the precipitate was dissolved in hydrochloric acid, and the presence of iron shown by potassium thiocyanate. This experiment was made in order to corroborate the theory that ferric molybdate is formed, and is slightly soluble in excess of alkali.

Effect of certain Metals on the various Methods.

In order to test the different methods when the metals commonly added are present, and also those which in future may be added, experiments were made with mixtures of the molybdenum and iron solutions, adding vanadium, tungsten, uranium, and chromium.

Separation of Iron by Sodium Hydroxide and Titration of the Molybdenum by Potassium Permanganate.—In making the following experiments, the operation was conducted under exactly the same conditions as used for the estimation of molybdenum, separating the iron by sodium hydroxide and titrating the reduced molybdenum by potassium permanganate, with the exception that the iron was not re-precipitated. The relative amounts of iron and molybdenum taken were those corresponding to the usual molybdenum steel. This relation was kept constant, and the amount of other metals varied.

Iron taken.	Molybdenum taken.	Molybdenum found.	Grm.
Grm.	Grm.	Grm.	Grm.
0.1076	0.00492	0.00856	0.00169
0.1076	0.00492	0.01867	0.00843
0.1076	0.00492	0.00716	0.00242
0.1076	0.00492	0.01074	0.01210
0.1076	0.00492	0.00545	0.00190
0.1076	0.00492	0.00749	0.00951
0.1076	0.00492	0.00560	0.00210
0.1076	0.00492	0.00560	0.01048

The vanadium added was pure V_2O_5 (containing 56.22 per cent of vanadium). The uranium salt was uranium nitrate, C. P., Kahlbaum (containing 47.57 per cent

* Read at the meeting of the New York Section of the American Chemical Society, January 8, 1904. From the *Journal of the American Chemical Society*, xxvi., No. 6.

uranium). The tungsten was added in the form of sodium tungstate. The amount of tungsten in the salt was determined by converting the sodium tungstate into tungsten trioxide, and weighing the ignited tungstic oxide in a porcelain Gooch crucible. The amount of tungsten present in the salt was found to be 60.49 per cent. The chromium was added as sulphate, obtained from pure chromic acid.

From the results obtained we see that vanadium, tungsten, and uranium all interfere with the method, chromium giving slightly higher results than those obtained where iron only is present.

The vanadium goes partly into solution, some being precipitated as a ferric vanadate with the iron, as shown by Pope ("Investigations of Magnetic Iron Ores from Eastern Ontario," *Trans. A. I. M. E.*, October, 1899, xxix., 372), and thus gives high results, being reduced with the molybdenum, and oxidised by the potassium permanganate during the titration of the molybdenum.

The uranium probably forms a uranyl molybdate, which is soluble in excess of alkali, and this is reduced to UO_2 and oxidised again to UO_3 , and gives high results. The filtrates from the ferric hydroxide, after adding sodium hydroxide, were yellow in colour.

Tungstates and tungstic acid are soluble in alkali, and, of course, are present with the molybdenum in the filtrate.

Separation of Molybdenum from Iron as Molybdenum Trisulphide by Hydrogen Sulphide under Pressure, and Titration with Potassium Permanganate.—In order to determine the effect of these metals upon the precipitation method by hydrogen sulphide under pressure, a series of experiments similar to the last were conducted. The experiments were pursued under the same conditions as for the determination of molybdenum in the absence of these metals, and the results obtained showed that neither vanadium, tungsten, uranium, or chromium interfered, even when the quantities were increased. In the case of tungsten 3 to 4 grms. of tartaric acid were added in order to keep the tungsten in solution, as in the method for the separation of tungsten from molybdenum by H. Rose (Treadwell, "Kurztes Lehrbuch der Analytischen Chemie," 1902, vol. ii., p. 187).

Iron taken.	Molybdenum found.	Molybdenum found.	
Grams.	Grams.	Grams.	
0.1076	0.00492	0.00529	0.00169
0.1076	0.00492	0.00498	0.00169
0.1076	0.00492	0.00498	0.00843
0.1076	0.00492	0.00529	0.00843
0.1076	0.00492	0.00498	0.01687
0.1076	0.00492	0.00482	0.00190
0.1076	0.00492	0.00529	0.00190
0.1076	0.00492	0.00513	0.00951
0.1076	0.00492	0.00544	0.01902
0.1076	0.00492	0.00560	0.00242
0.1076	0.00492	0.00498	0.00242
0.1076	0.00492	0.00529	0.01210
0.1076	0.00492	0.00513	0.01210
0.1076	0.00492	0.00498	0.00210
0.1076	0.00492	0.00482	0.01048

Amount of vanadium added.

Amount of uranium added.

Amount of tungsten added.

Amount of chromium added.

PART II.

A new method for the determination of molybdenum in steel and steel-making alloys was then devised, founded upon the foregoing results, and then tested by the analysis of a set of samples of molybdenum steels and alloys, and compared with a typical sodium hydroxide separation method, followed by titration with potassium permanganate, and the precipitation method as lead molybdate.

After considerable experimenting the following method was used for analysis:—

For Molybdenum Steel:—Dissolve about 1 gm. of drillings in 80 c.c. of "silicon mixture"—500 c.c. concentrated nitric acid, 150 c.c. concentrated sulphuric acid,

and 1500 c.c. of water (Phillips, "Methods of Iron Analysis, p. 116)—in a porcelain casserole, adding a little at first, as the action is violent. Evaporate to fumes of sulphur trioxide. Allow to cool, and add 50 c.c. of hot water, and heat to boiling in order to get the salts into solution. Pour the solution into a pressure bottle, and add 6 c.c. concentrated sulphuric acid. Dilute until the bulk of the solution is about 200 c.c., and pass a very rapid stream of hydrogen sulphide through the solution until the precipitate collects. Then close the bottle, and heat in a water-bath at 100° C. for from one to two hours. Allow to cool, empty the contents into a beaker, and wash out the bottle. Filter on a Gooch crucible, using suction, and wash with dilute sulphuric acid (1:50) saturated with hydrogen sulphide. Remove the precipitate and asbestos with a glass rod, and place in a small casserole, washing out the Gooch crucible with water. Add 10 c.c. concentrated hydrochloric acid, 5 c.c. concentrated nitric acid, and 10 c.c. concentrated sulphuric acid, and evaporate to very copious fumes of sulphur trioxide, blowing air through the solution. Allow to cool, add 50 c.c. of water, then ammonia in excess, and filter out the asbestos, and a little ferric hydroxide. Wash thoroughly with hot water. The filtrate is then acidified, run through a reductor, and titrated with potassium permanganate, using the same conditions as for standardising the permanganate solution.

For Ferro-molybdenum.—Dissolve 4 to 5 grms. of ferro-molybdenum in 180 to 200 c.c. "silicon mixture," pour the solution into a standard litre flask, and dilute to the mark when cold. Take out portions of 50 c.c. or 100 c.c., and evaporate to fumes of sulphur trioxide, and proceed as in the case of molybdenum steel.

For Molybdenum Metal.—Dissolve 2 to 3 grms. of metal in "silicon mixture," add concentrated hydrochloric acid, and heat for some time. Dilute with water, and filter into a litre flask. Burn the filter, moistened with nitric acid in a platinum crucible, using as low a heat as possible, and fuse the residue with potassium pyrosulphate. Dissolve the melt in hot water, and add it to the solution in the flask. Allow to cool, and dilute to the mark. Take out portions of 50 c.c., and proceed as in the case of molybdenum steel.

Tungsten, if present, separates out partially as tungstic oxide when the solution is evaporated to fumes of sulphur trioxide. This may be tested for by dissolving it in ammonia, making strongly acid with hydrochloric acid, adding a saturated hydrochloric acid solution of stannous chloride, and then ammonium or potassium thiocyanate. A deep green colour shows tungsten. Molybdenum, under similar conditions, gives a deep red colour.

It is very important to note that tungsten trioxide is quite soluble in acids, although otherwise stated by most authorities (Corney's "Dictionary of Solubilities," p. 438; Storer's "Dictionary of Solubilities"; Watts's "Dictionary of Chemistry."

When tungsten is present, after dissolving the steel in the "silicon mixture," and evaporating to fumes of sulphuric trioxide, allow to cool, add 50 c.c. hot water, 5 grms. of tartaric acid, and heat to boiling. Filter into the pressure bottle, and wash the residue with hot water. Then wash the residue back into the casserole, and repeat the treatment with "silicon mixture" and tartaric acid as before. Filter again into the pressure bottle, and when washed proceed as already described.

"Silicon mixture" was found to be the best solvent for molybdenum steels and ferro-molybdenums, and was also used because it is a common reagent at the steel works. When tungsten was present it was found necessary to re-treat the residue, as it contains a little molybdenum.

In titrating with potassium permanganate, the conditions used were those given by Miller and Frank (*Journ. Am. Chem. Soc.*, 1903, xxv., 919). Length of column of unamalgamated zinc (20 to 30 mesh), 15 inches; time of passage, six minutes; temperature, 70–75° C.; volume of solution, 200 to 250 c.c.; acidity, 10 c.c. concentrated sulphuric acid; and titrated immediately. The following

percentages of molybdenum were obtained by these methods:—

Molybdenum steel	3.63	3.62	3.595	—
Molybdenum-chromium steel ..	4.02	4.11	4.09	—
Molybdenum-vanadium steel ..	9.11	9.12	9.26	—
Molybdenum - chromium - tungsten steel	3.47	3.51	—	—
Ferro-molybdenum	44.50	44.57	44.72	—
Ferro-molybdenum, high in sulphur	34.18	34.24	34.42	34.49
Molybdenum metal	83.84	84.00	84.00	84.16

In analysing the molybdenum-chromium-tungsten steel the residue was not filtered out at first, and the results obtained for percentages of molybdenum were 4.06 per cent, 4.04 per cent, and 3.97 per cent, due to small amounts of tungsten which were dissolved by the acids when making the final evaporation with sulphuric acid. The solution was filtered and washed before the addition of ammonia.

In order to compare this method with those now in general use, the same samples were next analysed by the latest modification (*Iron Age*, Nov. 20, 1902; *Journ. Am. Chem. Soc.*, 1903, xxv., 215) of the method of Kopp, Brakes, and Auchy, which is in brief as follows:—Dissolve 0.8 gm. of drillings in a mixture of 15 c.c. dilute nitric acid, 10 c.c. concentrated hydrochloric acid, and 3 c.c. concentrated sulphuric acid. Keep covered. Evaporate to fumes, which must be very dense, being careful that no nitric acid remains on the cover. Boil the residue with 50 c.c. water. Allow to cool, and pour by degrees with shaking into 100 c.c. of caustic soda solution (1 pound of caustic soda in 2000 to 2100 c.c. water). Dilute up to 200 c.c. (by 200 c.c. graduated Erlenmeyer flask), mix well by shaking, and allow to settle. Filter through a dry filter into a 100 c.c. measuring flask, till mark is reached, add 15 c.c. of concentrated sulphuric acid, reduce, and titrate.

The percentages of molybdenum obtained were as follows:—

Molybdenum steel	3.91	3.92	4.08
Molybdenum-chromium steel ..	4.28	4.37	4.43
Molybdenum-vanadium steel ..	11.72	11.63	11.96
Molybdenum-chromium-tungsten steel ..	6.21	6.26	6.30
Ferro-molybdenum	46.78	46.93	47.01
Ferro-molybdenum, high in sulphur ..	36.21	36.26	36.32
Molybdenum metal	86.58	86.58	86.88

In reducing and titrating the molybdenum in the foregoing samples, the conditions just described for reducing and titrating were followed.

From the results we see that when molybdenum, or molybdenum and chromium, are present, the results are high, due to the formation of a ferric molybdate, which is slightly soluble in the large excess of alkali. The method has the advantage of being very rapid. Three c.c. of concentrated sulphuric acid is too small an amount when evaporated to fumes of sulphur trioxide in order to get rid of all other acids. Eight to 10 c.c. are preferable. A defect in the method is the addition of 15 c.c. of concentrated sulphuric acid to the alkaline filtrate, containing molybdenum for reduction and titration. No correct results can be obtained in reducing and titrating molybdenum, unless the same conditions are followed in analysing the steel as are used for standardising the permanganate solution. The amount of free acid should be kept constant. The solution should be made neutral, and then a definite quantity of concentrated sulphuric acid added in excess.

If tungsten, vanadium, or uranium be present, the method is worthless, as they will be obtained in the filtrate with the molybdenum, and will be reduced and re-oxidised by the permanganate.

The next method used was that of Ibbotson and Brearley, as given in their "Analysis of Steel Works Materials," p. 84, slightly modified to obtain more correct results, by statements made previously by them in the *CHEMICAL NEWS*, (1900, lxxxi., 269), i.e., re-precipitating the lead molybdate to get rid of silica and any other impurity. The method used was as follows:—

Dissolve 2 grms. of the sample in hydrochloric acid and oxidise by nitric acid or potassium chlorate. Add sodium carbonate, taking care to stop the addition short of the production of a red colour or precipitate. Pass through a small pulp filter, and place the filter in a flask containing 30 to 40 c.c. more of double normal caustic soda than is necessary to precipitate the whole of the iron.

After disintegrating the added filter, which may possibly contain a little tungstic or molybdic oxide, heat the contents of the flask to boiling, and add the hot solution, shaking constantly. Make up to 500 c.c., filter off 250 c.c., add a drop of methyl orange, and a decided excess of hydrochloric acid, then an excess of lead acetate solution (40 grms. of crystallised lead acetate per litre), and more than enough ammonium acetate to destroy the free hydrochloric acid. Heat the solution to boiling, allow to settle, filter, wash with hot water, ignite, and weigh the lead molybdate.

In carrying out this method, difficulty was first encountered in dissolving the steels, as hydrochloric and nitric acids are not the best solvent for a molybdenum steel, and in the case of the samples of ferro-molybdenum it was found impossible to get them into solution completely by the use of hydrochloric and nitric acids. In adding sodium carbonate, it is difficult to get the solution at the right point of acidity. If left too acid, there will not be enough sodium hydroxide to separate the iron and the molybdenum, as only a small excess is used.

Great difficulty was encountered at this point, on account of the reddish colour of the steel solution. By increasing the strength or amount of sodium hydroxide added, this could be remedied. This would also obviate the necessity of filtering the solution of the steel, and treating the residue separately.

In precipitating the molybdenum as lead molybdate, a decided excess of hydrochloric acid is first added, and then this excess of hydrochloric acid is destroyed by the addition of ammonium acetate. If there is a large excess of hydrochloric acid present, there will be a large excess of acetic acid present, and this affects the precipitation of lead molybdate (Brearley, *CHEMICAL NEWS*, 1893, lxxviii., 203). By first neutralising the acid with ammonia, and then adding 2 to 3 c.c. of acetic acid (33 per cent) in excess, the best conditions for precipitation are obtained.

In analysing the molybdenum-chromium-tungsten steel, the following modification of the method was used (Ibbotson and Brearley's "Analysis of Steel Works Materials," p. 85):—Dissolve the ignited lead salts in hydrochloric acid, add a few drops of nitric acid, and evaporate nearly to dryness. Add 100 to 200 c.c. of dilute hydrochloric acid (1:4), boil, and filter off the tungstic oxide. The molybdenum is re-precipitated from the filtrate with lead acetate, &c.

It is claimed that an accurate separation of the two oxides from their lead salts can be made in this manner, no matter in what proportion they exist. The percentage results obtained were as follows:—

Molybdenum steel	3.84	3.68	—
Molybdenum-chromium-tungsten steel ..	4.31	4.43	4.44

The precipitates of ferric hydroxide from the molybdenum steel were dissolved in acid after thorough washing, and the iron precipitated again by a large excess of sodium hydroxide (200 c.c. of 54 normal sodium hydroxide), and the filtrates precipitated with lead acetate as before. The results were 3.93 and 3.90 per cent of molybdenum, showing that the molybdenum had not been completely separated from the iron.

In analysing the molybdenum-chromium-tungsten steel, the results are about 0.9 per cent high, due to tungsten, as tungstic acid is not precipitated completely by boiling to a small volume with acid.

The results obtained on the molybdenum-chromium steel were very low, the molybdenum not being completely separated by the small amount of alkali used.

Vanadium interferes with the lead molybdate precipitation, as stated by Ibbotson and Brearley.

9. The sulphide precipitation, followed by reduction and titration with potassium permanganate, not only gives accurate results, but has the great advantage that nothing which is present in steels, ferro-molybdenum, or molybdenum metal, interferes with the accuracy of the results.

When rosaniline trichlorhydrate is dissolved in mineral acids, there is a secondary phenomenon, lasting for eight minutes, in which the liquid loses its red colour and heat is evolved. The reaction takes place in an inverse sense, an equivalent quantity of heat being absorbed when rosaniline carbinol is dissolved in acetic acid. The colourless compounds were formerly thought to be carbinol salts, $(\text{HCINH}_2\text{C}_6\text{H}_4)_3\text{COH}$. Further work has, however, convinced the author that the colourless compounds are the new cyclohexane salts. He thus arrives at the following conclusions:—1. The fuchsines, treated with excess of mineral acid, take up 4 molecules of water; the quinone nucleus is transformed into the hexahydrobenzene nucleus, and colourless solutions of tetraoxycyclohexanerosaniline trichlorhydrate are formed. 2. In the neutralisation of the rosaniline carbinols by an acid, the benzene nucleus always first passes into the hexahydrobenzene nucleus before finally being transformed into the quinone nucleus.

New Work.—Prof. Raphael Meldola is to be congratulated on the completion of Volume I. of "The Chemical Synthesis of Vital Products and the Interrelations between Organic Compounds," upon which he has been engaged since 1895, and which is to be published by Mr. Edward Arnold on November 1st. This important work, containing, as it does, in the most accessible form, the net results of modern research in the department of synthetical chemistry up to the moment of going to press, will be of the utmost value to investigators in this field both at home and abroad.

MEETINGS FOR THE WEEK.

WEDNESDAY, Nov. 2nd.—Society of Public Analysts, 8. "Detection and Estimation of Small Quantities of Maltose in the presence of Dextrose," by J. L. Baker and W. D. Dick. "Use of Palladium-hydrogen as a Reducing Agent in Quantitative Analysis," by A. C. Chapman. "Some Recent Abnormal Milk Results," by S. Harvey.

THURSDAY, 3rd.—Chemical, 8. "Note on the Action of Nitric Acid on the Ethers" by J. B. Cohen and J. Gatecliff. "Condensation of Formaldehyde with Acetone," by E. A. Werner. "Union of Hydrogen and Chlorine—Rate of Decay of Activity of Chlorine," by J. W. Mellor. "Action of Phthalic Anhydride on α -Naphthyl-magnesium Bromide," by S. S. Pickles and C. Weizmann. "Constitution of Nitrogen Iodide," by O. Sikerrad. "Available Plant Food in Soils," by H. Ingle. "Combustion of Ethylene," by W. A. Bone and R. V. Wheeler. "Decomposition of Methylurea," by C. E. Fawcitt. "Influence of certain Salts and Organic Bodies on the Oxidation of Glucose," by Miss E. G. Wilcock. "Influence of Potassium Persulphate on the Estimation of Hydrogen Peroxide," by J. A. N. Friend. "Dynamic Isomerism of α - and β -Crotic Acids," by R. S. Morrell and E. K. Hanson. "Influence of Sunlight on the Dissolving of Gold in an Aqueous Solution of Potassium Cyanide," by W. A. Caldecott. "Fractional Hydrolysis of Amygdalinal Acid" and "Isoamylglycoline," by H. D. Dakin.

IMPORTANT NEW SCIENCE BOOKS.

MATERIEN DER STEREOCHEMIE. Ed. C. A. BISCHOFF. 2 stout vols., 8vo, covering the period from 1894 to 1902. 54 10s.

PAULI (Dr. R.)—DIE SYNTHESER DER AZOFARBSTOFFE auf Grund eines symbolischen Systems. Large 8vo. £1 10s.

WOLFRUM (Dr. A.)—CHEMISCHES PRAKTIKUM. 2 vols. 8vo, and an ATLAS in folio containing 721 ill. and 11 plates. Cloth, £1 18s.

TRAITE DE CHIMIE MINERALE. Published under the Direction of HENRI MOISSAN, with the collaboration of the greatest Scientific Men. Vols. I and III. To be completed in 5 vols. Subscription Price for the whole work, £2 8s., which will be raised Dec. 1, 1904. Any other BOOKS and PERIODICALS (English and Foreign) reviewed in this Paper promptly supplied.

A. OWEN & CO.,

English and Foreign Science Booksellers and Publishers.
286, HIGH HOLBORN, LONDON, W.C.

MELTING & BOILING-POINT
TABLES.

BY

THOMAS CARNELLEY,

D.Sc. (Lond.), B.Sc. (Vict.), F.C.S.,

Professor of Chemistry in University College, Dundee.

The Standard and only work upon the subject.

2 Vols. Ry. 4to. 799 pp. 42s.

HARRISON & SONS, Pall Mall, London, S.W.

E. GEORGE & SONS,
BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.

Are OPEN to PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased. Current Catalogue of General Literature sent on application.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC, As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, L. THARGE, SHOT, &c.

UNIVERSITY OF BIRMINGHAM.

ASSISTANT LECTURER AND DEMONSTRATOR IN
CHEMISTRY.

The Council invites applications for this
Appointment.

The stipend will be £750 per annum.

The Candidate selected will be required to enter on his duties at the earliest possible date. Further particulars may be obtained from the undersigned, to whom applications, accompanied by testimonials, should be sent not later than November 7th, 1904.

GEO. H. MORLEY, Secretary

UNIVERSITY OF GLASGOW.

ADDITIONAL EXAMINERSHIPS.

The University Court of the University of Glasgow will shortly proceed to appoint the following additional Examiners:—

(a) For Degrees in Arts and Science.—One Examiner in MATHEMATICS. Annual salary, £70.

(b) For Degrees in Arts, Science, and Medicine.—One Examiner in NATURAL PHILOSOPHY (including PRACTICAL PHYSICS). Annual salary, £70. Candidates should be qualified both on the Mathematical and Experimental side. One Examiner in CHEMISTRY. Annual salary, £50.

The appointments will be for three or four years from January 1st, 1905, and, in addition to the above-mentioned salaries, hotel and travelling expenses will be paid.

Candidates should lodge twenty copies of their application and testimonials with the undersigned on or before November 12th, 1904.

ALAN E. CLAPPERTON,
Secretary, Glasgow University Court,
91, West Regent St., Glasgow.

INSTITUTE OF CHEMISTRY
OF GREAT BRITAIN AND IRELAND.

Incorporated by Royal Charter.

NOTICE IS HEREBY GIVEN that the next INTERMEDIATE EXAMINATION will be held at the Laboratories of the Institute, commencing on TUESDAY, the 3rd of JANUARY, 1905.

Examinations in the following branches of the FINAL EXAMINATION for the ASSOCIATESHIP (A.I.C.) will be held in the Laboratories of the Institute, commencing on either TUESDAY, the 3rd, or TUESDAY, the 10th of JANUARY, 1905:—(a) Mineral Chemistry; (b) Metallurgical Chemistry; (c) Physical Chemistry; (d) Organic Chemistry. A Final Examination in Branch (e) The Analysis of Food and Drugs and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, will be held in the Laboratories of the Institute, commencing on MONDAY, the 9th day of JANUARY, 1905.

The Examinations are open only to Candidates who have complied with the Regulations.*

Applications for admission to the above Examinations should be forwarded to the Registrar not later than THURSDAY, the 1st of DECEMBER, 1904, on which day the List of Candidates will be closed. (By Order of the Council)

RICHARD B. PILCHER,
30, Bloomsbury Square, London, W.C., Registrar and Secretary.

* The Book of Regulations for the Admission of Students, Associates, and Fellows may be obtained on application to Messrs. Blondell, Taylor, and Co., 173, Upper Thames Street, London, E.C. Price One Shilling.

PLATINUM UTENSILS, SCRAP,
LAMP-ENDS, &c.,

Purchased at highest prices by—
DERBY & CO., LTD., 44, CLERKENWELL ROAD, LONDON.
N.B.—Platinum Sold.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

THE CHEMICAL NEWS.

VOL. XC., No. 2345.

NOTE ON THE HIGHER GLYCERIDES.*

By J. B. HANNAY, F.R.S.E., F.I.C.

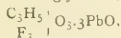
It has long been known that oxide of lead can be dissolved by heat in linseed oil, as it has been so employed to improve the "drying" qualities of the oil. Some qualitative experiments conducted in the year 1895 showed me that this power of dissolving oxide of lead was common to all the higher glycerides, and also that they took up a fixed quantity and formed, not mere solutions, but true chemical compounds. As the compound yielded a lead soap and glycerin on treating its ethereal solution with water in the cold, it seemed to offer a means of throwing further light on the course of saponification of the glycerides.

It was found that on heating tristearin, triolein, trilinolein, and triricinolein, as represented by purified stearin, olive oil, linseed oil, and castor oil, as also rape, cotton-seed, and earth-nut oils, with dry litharge in fine powder, at a temperature of from 165° to 180°, combination took place, the oxide of lead being gradually dissolved and the liquid becoming more and more viscid until, after two hours' heating, rising to a temperature of 180° to 190°, saturation seemed to be attained, and the result was a wax-like body, viscid when hot, and which, on cooling, formed a brittle solid like Carnauba wax, and which did not adhere to glass.

The compounds formed (except that formed from stearin, which is less soluble) were very soluble in liquid paraffins and olefines, and many hydrocarbons, such as benzole, toluol, xylol, and also in carbon tetrachloride and disulphide, chloroform, amyl acetate, and glacial acetic acid, but practically insoluble in alcohol and acetone.

By washing with acetone, or precipitating the compound from its chloroform solution by acetone or alcohol, the new compounds may be freed from uncombined oils. The solubility of both the oleic and linoleic compounds is so great that most of the solutions show no saturation-point, but the solid and solvent are miscible in all proportions.

An analysis of the products, separated from free litharge and oil by solution in chloroform, filtration, and precipitation by acetone, gave metallic lead to the extent of from 36 per cent in the rape oil compound to 41 per cent in the case of the linseed oil compound; other oils yielding compounds between those limits. This gives three atoms of lead to each molecule of triglyceride, or a formula of—



where $\bar{\text{F}}$ represents the radicle of one of the fatty acids.

Evidently, then, the lead was in some relation to the acid radicle, but as the acid had the hydrogen of its carboxyl removed by combination with the glyceryl radicle, the combination must be quite other than the formation of a salt of the acid, as in "saponification."

An examination of the reaction for the evolution of water was made by mixing 20 grms. of dried olive oil with 25 grms. of litharge which had been heated to 250°. These were combined at 180°, and a slow current of dried carbon dioxide passed over the mixture, and any moisture collected as usual by a tube with pumice saturated with strong sulphuric acid. The loss of weight after combination was 0.235 gm., while the gain in weight in the drying tube was only 0.072, showing that no moisture was evolved, and that the loss of weight was due to small quantities of essential oil, &c., present in the olive oil; so that the reaction was a direct combination of the glyceride with the oxide of lead.

Experiments showed that this combination begins to

take place slowly with stearine at 160°, but cannot be completed at that temperature. With triolein it commences about 130, and with trilinolein as low as 87° there is some action, the chemical activity being thus greater as the glyceride acids are of a less saturated type. Ordinary ground fused litharge did not act as quickly as that produced by carefully dehydrating lead hydrate, which produces a light flocculent litharge, very finely divided, and it was with oxide thus prepared that all the experiments quoted were done.

It was found that the same glycerides acted upon dry lead carbonate when raised to a temperature of 166°, and the same compounds were formed. At this temperature lead carbonate is not decomposed by heat alone, and as the glyceride attacks the carbonate with strong effervescence, it is apparent that we have true chemical action. When an excess of lead carbonate was used, the unchanged carbonate representing the excess was recovered in full by dissolving the compound in ether, chloroform, or petroleum spirit, and filtering.

Experiments were made with the above oils using an excess of lead carbonate, and the carbon dioxide was absorbed and weighed, and a drying tube placed to retain any water; but in no case was any appreciable amount of water given off. These weights were checked by the loss of weight of the flask and contents, and were found to agree fairly well.

Two typical experiments may be quoted—one with olive oil and the other with linseed—triolein and trilinolein:—

Oleic taken		20.703 grms.
Lead carbonate		36.276 "

Theory for
olein + 3PbO.

Carbon dioxide collected		3.127	3.051
Collected in H ₂ SO ₄ tube (trace H ₂ O)		0.014	0.000
Total loss of weight		3.155	3.091
Carbonate of lead recovered		17.392	17.578
Weight of compound formed		36.675	36.350

The oils were dried by heating to 105°, and the carbonate of lead to 100°, while in the experiments with litharge the latter was heated to about 300°.

In the case of the linolein experiment and several other oils, the result was checked by dissolving the compound in ether, shaking with water, and separating; the operation being repeated several times to extract all the glycerin. It was found to be difficult to obtain the last traces of glycerin in this way, so the lead salt was generally decomposed by sulphuric acid, and the excess of acid removed by barium carbonate, and the glycerin estimated. The following is a typical result:—

Theory for
3PbO.

Linolein taken		8.705	—
Carbonate of lead dissolved		7.890	7.938
Carbon dioxide collected		1.221	1.308
Water and volatile matter		0.012	0.000
Total solid was obtained		14.92	15.337
Glycerin		0.84	0.912
Basic linoleate of lead		14.39	14.693

It was found that if the heating were long continued and carried up to about 200°, it was possible to obtain a lead compound with 2 to 3 per cent excess of lead, but in these cases the compound was very dark in colour, and the action had been pushed too far.

When heated to 180° and kept till saturated, say, for two hours, and extracted with benzene, chloroform, or other anhydrous solvent, the compound had a perfectly constant composition, as shown by the subjoined analyses.

The method of estimating the lead was that of incinerating in a porcelain crucible and burning off any free carbon, then passing hydrogen through a pipe in the cover to reduce any oxide of lead, and weighing the metallic lead. The lead is obtained in this way in bright metallic beads. A portion of the compound was distilled to ascertain if any lead were volatilised during the driving off of the volatile

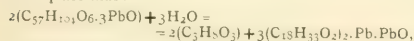
* The substance of a Paper read before the Chemical Society.

The two hydrogen atoms which replace the lead when water is added and enable the complex molecule to break

up into glycerin and oleic acid, are shown in parenthesis, and the additive compounds formed by bromine, sulphur chloride, or oxygen are also indicated. The compound may be formulated more simply, and the tie formed by the divalent lead shown as—



where 3 of divalent lead replace 6 of hydrogen—3 in the glycerol and 3 in the oleic acid,—thus linking the glyceryl and oleic radicles together. The decomposition by water takes place thus:—



yielding glycerin and a basic oleate of lead.

These two reactions—the combination of the dry oxide of lead with the tri-glyceride and the subsequent decomposition with water—are probably the true steps of the saponification of oils by boiling with litharge and water—the process used in making lead soaps from time immemorial, and by which glycerin was originally manufactured.

(To be continued).

REPORT OF COMMITTEE ON THE
CADIUM CELL.

*To the Board of Directors of the American Institute of
Electrical Engineers.*

THE committee appointed by you to report on the preparation of materials and the construction of the cadmium or Weston cell has made very substantial progress, and begs leave to make the following preliminary report, with the request that the Committee be continued.

The most serious variations in the electromotive force of both Clarke and Weston standard cells have been traced to the influence of the mercurous sulphate. (See *Zeit. für Instrumentenkunde*, February, 1901, and the "Report of the National Physical Laboratory of England" for 1903). The problem of ascertaining the cause of these variations and the development of a standard method of preparing the mercurous sulphate was accordingly taken up by the Chairman of this Committee in conjunction with Dr. George A. Hulett, of the Department of Chemistry in the University of Michigan.

The method of preparation in use by the European manufacturers of mercurous sulphate consists in its precipitation

TABLE 1.—D Cells.

Date.		1.	2.	3.	4.
		roigio	roigio	roigio	roigio
Jan.	5, 21 ¹⁰	08	09	09	09
	6, 21 ¹¹	08	08	085	09
	7, 21 ¹¹	07	08	08	08
	9, 21 ¹¹	07 +	07	07	08
	11, 21 ¹¹	07	06	07	075
	14, 21 ¹¹	06	065	07	07 +
	16, 21 ¹¹	07	06	07	07
	23, 21 ¹¹	065	065	07	075
Feb.	1, 21 ¹⁰	07	08	08	085
	13, 21 ¹¹	07	08	08	08
	16, 21 ¹¹	07	07	08	08 +
	18, 21 ¹¹	07	08 +	09	09
	22, 21 ²⁰	07	085	085	09
	25, 21 ²⁰	07	07	075	08
March	1, 21 ¹¹	07	07	075	08
	5, 21 ²⁰	07	07	075	08
	12, 21 ¹⁰	07	07	07	07 +
	15, 21 ¹¹	07	07 +	07	075
	17, 21 ²⁰	06	065	07	07

TABLE II.—F Cells.

Date	1	2	3	4	5	6	7	8	9	10
February 15, 21.1	1.01907	1.01907	1.01907	1.01908	1.01908	1.019065	1.01907	1.01908	1.01905	1.01907
16, 21.1	065	06	07	08	07	06	06	07	07	065
17, 21.1	07	07	07	08	07	06	075	07	075	07
20, 21.1	07	07+	075	08	08	08	075	07	08	075
22, 21.2	075	08	08	08	08	08	08	08	08+	085
25, 21.0	08	08	08	08	085	085	08	08	09	08
March 1, 21.1	08	08	08	08+	08	08	08	08	08+	08
3, 21.2	08	08+	08	08+	08	08	08	08	08	08
12, 21.0	075	08	08	08	08	08	08	08	08	08
15, 21.1	08	085	09	09	08	08	08	08	08	08
17, 21.3	075	08	08	08	08	08	08	085	085	09
21, 21.3	07	07+	08	075	08	07	07+	08	08	08
23, 21.3	07	075	08	075	07	07	07	075	08	08
25, 21.0	075	08	08	085	08	075	075	08	08	08
April 2, 21.2	07	07+	08	08	08	075	08	08	08+	08
5, 21.1	075	08	08	08	08	075	08	08	08	08
9, 21.0	08	08	085	08	09	08	08+	08	08	08
16, 21.0	08	085	085	08	085	07	08	08	085	08
28, 21.1	07	075	08	08	08+	08	08	08	08	08

by bringing together a solution of mercurous nitrate and sodium sulphate or sulphuric acid. This method has been repeated with a number of variations, and the various preparations give variable results when used in the cadmium cell, and all of them higher electromotive force than the mercurous sulphate prepared electrolytically, as described below. These results suggest that perhaps mercurous sulphate might carry isomorphously a small quantity of mercurous nitrate, since both of these salts crystallise in the monoclinic system. In fact, Dr. Hulett has detected the nitrate in commercial preparations, and in some of those made by himself. A cell set up with mercurous sulphate of the standard preparation, to which a trace of mercurous nitrate had been added, showed an increased electromotive force due to the nitrate. Not only does the presence of the nitrate raise the electromotive force of the cell, but the relative amount of the nitrate present appears not to be invariable.

In view of these facts, a new and standard method of making mercurous sulphate from pure mercury and dilute sulphuric acid appeared to be highly desirable. Such a method has been devised by Dr. Hulett; and independently by Dr. Wolff, of the Bureau of Standards. (See paper by Henry S. Carhart and George A. Hulett in the *Transactions of the American Electrochemical Society*, vol. v.; also one by F. A. Wolff, same volume).

A new electrolytic method of preparing the cadmium amalgam, and one for washing the mercurous sulphate to remove the acid without the use of pure water, were also devised. (See specifications below). The results are highly satisfactory, and cells made in accordance with the specifications appended to this report show remarkable agreement and constancy. Your Committee is well satisfied that the principal difficulties in making Weston cells have now been removed.

The two curves in Fig. 1 show the behaviour of two cells for forty days after they were placed in a constant temperature bath, at 21.1°C . Cell D 6 was made with mercurous sulphate prepared in the old way by precipitation; cell D 1 was made with the same materials, except that the electrolytic mercurous sulphate was used. Comment is unnecessary. The electromotive forces given are relative and not absolute.

The accompanying tables exhibit measurements made on cells D 1 to D 4, and F 1 to F 10, all of them set up with the electrolytic mercurous sulphate. The figures were obtained by comparison with an old cell, B 7, by means of a Wolff's potentiometer and a type "H" d'Arsonval galvanometer made by Leeds and Northrup. The fifth decimal place could be read with the greatest ease.

In determining the effect produced by changing a single feature in the preparation of the materials, about 100 cells of the H-form have been made and tested. These are still under observation. All of them, except the first ten, have been hermetically sealed. The sealing is readily effected by making the glass containing cell of a special form, and sealing with two blast lamps.

The Committee offers the following specifications, which are to be considered as provisional only, for the preparation of the cadmium cell with saturated solution and excess of crystals of cadmium sulphate. For the cell so prepared the Committee would suggest the name, "Weston Normal Cell."

1. Mercury.

Mercury free from grease should be first shaken with a nitric acid solution of mercurous nitrate (*Zeit. Phys. Chem.*, xxxiii., 611), and, after drying, it should be distilled in a vacuum at least twice.

2. Cadmium Sulphate Solution.

The best pure commercial salt is dissolved at room temperature in its own weight of distilled water, with the aid of a motor-driven stirrer. The solution must be filtered until perfectly clear; it may then be placed in a large crystallising dish in a small room free of dust; it is of advantage to remove the water vapour by appropriate

drying agents. The slow ensuing crystallisation should yield perfectly transparent crystals. After about two-thirds of the water has evaporated, the mother-liquor is poured off, and only the clear crystals are taken; those that are white are re-dissolved and added to the mother-liquor. The whole is then filtered, and left to crystallise again. The selected clear crystals are rinsed with distilled water, drained, and left to dry.

To make a solution of cadmium sulphate for setting up cells, the pure crystals are put into an Erlenmeyer flask and covered with two-thirds their weight of distilled water. A suitable stirrer (Schultz stirrer, *Ber.*, 1896, 2883) is driven by a motor, for the purpose of causing the water to circulate over the crystals, for at least half a day, preferably in a bath at 25°C ., controlled by a thermostat. The supernatant liquid should be clear, and should remain so indefinitely. It should be left standing over the crystals, and when it is used it should be saturated at a temperature as high as 25°C . The saturation of the solution is of great importance in order that the cells may quickly reach electrical equilibrium.

3. Cadmium Amalgam.

To prepare a 12.5 per cent cadmium amalgam, free from zinc, a large crystallising dish is nearly filled with a saturated solution of cadmium sulphate slightly acidulated with sulphuric acid. In a small low crystallising dish is placed a weighed quantity of pure mercury, and the whole is immersed in the cadmium sulphate solution. The pure cadmium of commerce is melted down into a large button with a stick of cadmium attached for electrical connection; or several of the cadmium rods, bound together, are placed in a vertical position with their lower ends in the solution, and beneath them a small low crystallising dish. If the cadmium disk or button is used, it is placed in the second low crystallising dish, which retains the finely divided dross or powder. The metallic cadmium is then made the anode and the mercury the cathode, connection with the latter being made by means of a platinum-wire sealed, except at its end, in a glass tube. The fall of potential from the anode to the cathode should not exceed 0.3 volt. An ammeter should be used to keep account of the quantity of electricity flowing through the cell, until something more than the necessary weight of cadmium has been deposited on the mercury cathode. The small crystallising dish, containing the cadmium amalgam, and some of the solution, is then removed and warmed over a bath till the amalgam melts under the cadmium sulphate solution. When cool it forms a crystalline disk. This method yields an amalgam free from zinc, and there is no oxide or dross formed, as there is when the amalgam is made by the method of heating. The solid amalgam should next be washed, dried on filter-paper, and weighed. The necessary weight of mercury to make a 12.5 per cent amalgam is finally added. The amalgam should be kept under a pure cadmium sulphate solution, and it must be melted on a water-bath to insure homogeneity before it is used in making a cell.

4. Mercurous Sulphate.

In a flat-bottomed glass vessel or deep crystallising dish place pure re-distilled mercury 2 c.m. or more deep. Cover with dilute sulphuric acid (one of acid to six of water) to a depth of 8 or 10 c.m. Make electrical connection with the mercury as the anode by means of a platinum wire covered, except at its end, by a glass tube. For a cathode use a piece of sheet platinum 50 as to expose to the acid solution a surface of about 50 sq. c.m. A current density of 0.5 ampère per 100 sq. c.m. surface of mercury may be used. A crystalline mercurous sulphate forms soon after the current begins to flow from the mercury to the acid solution. A stirrer, consisting of a glass rod bent at right angles at the bottom, must be used to keep the mercury surface exposed. The foot of the stirrer must pass close to the mercury, and the stirrer must be driven rapidly by a motor to keep the mercury agitated.

A little over 4 grms. an hour can be prepared in this way with a current of half an ampère. The mercurous sulphate formed should be protected from the light, since mercurous sulphate darkened by exposure to light gives too high an electromotive force. The sulphate will be white or grey, according to the amount of finely divided mercury mixed with it. The presence of this mercury in a state of fine division is a distinct advantage. If the stirring is continued after the circuit is broken, the crystals of mercurous sulphate grow in size, become whiter, and subsequent treatment is easier.

The mercurous sulphate may be removed from the mercury by a separatory funnel. It should be kept under the acid solution, one to six, in contact with mercury and in the dark.

3. The Paste.

When ready to fill a cell, the mercurous sulphate, which has been kept in contact with mercury under dilute sulphuric acid, is brought into a Gooch crucible of about 25 c.c. capacity (about three-fourths), avoiding much free mercury, which interferes with the filtering. A tiny filter paper covers the perforations in the bottom of the crucible, and the whole is mounted on a Bunsen filter flask and attached to a filter pump.

The mercurous sulphate is first washed a couple of times with dilute sulphuric acid (15 c.c. concentrated acid to a

without splashing. It should always be wiped with a filter paper or clean cloth before it is introduced into the cell.

The mercury, the thin paste, and the concentrated cadmium sulphate solution may be introduced in the same manner. An alternative method is to fill the cell through little funnels made out of small test-tubes. They must pass through the neck at *a*, and reach well down toward the bottom. After the mercury and the paste have been introduced, both legs of the cell are filled with clean, dry crystals of cadmium sulphate. Enough of the saturated cadmium sulphate solution is finally added to fill the cell to the top of the cross connecting tube.

The sealing off is readily done by means of two small horizontal blast flames, 5 c.m. long, directed in a line toward each other and just meeting. The narrow part at *a* is brought between the impinging flames, the glass quickly softens, and the top part is drawn off. A cell sealed in this way contains nothing but the necessary materials of the voltaic combination. It cannot leak, and can be immersed in a kerosene bath without danger that the oil will penetrate into the inside, as it does with sealing wax and paraffin.

After soldering copper wires to the platinum terminals of the cell, it is desirable to tie them securely with thread to the legs of the cell, as a precaution to avoid the

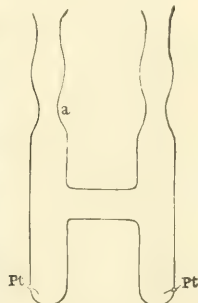
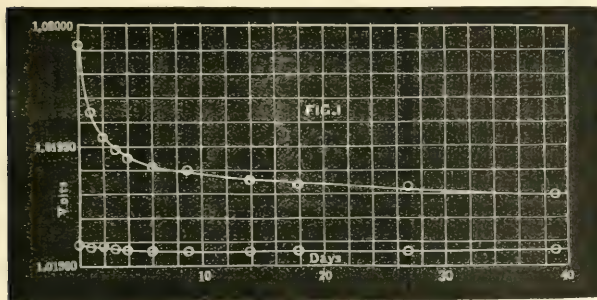


Fig. 2.

litre of water), and then with the saturated cadmium sulphate solution. The washing with the cadmium sulphate solution should be repeated five or six times to remove all the acid; only a few c.c. of the solution are needed for a single washing; after each washing the cadmium sulphate solution is to be removed as completely as possible by the filter-pump. The last washing leaves the salt ready to be made into a paste. The top layer after the last washing should be rejected.

The paste is then made in a clean agate mortar by grinding together crystals of the pure cadmium sulphate and a little mercury, and then mixing in about three volumes of the mercurous sulphate; finally add enough saturated cadmium sulphate solution to make a thin paste.

6. Construction of the Cell.

The H-form of cell is the most convenient to fill. Fig. 2 shows the glass cell half actual size, ready to be filled. The tubing is drawn out and contracted at *a* so as to leave the diameter about 6 c.m. and with thin walls at this point. The amalgam is melted over a water-bath and is introduced by means of a small tube, slightly contracted at the end, and of a diameter that will allow it to pass freely through the neck *a*. The warmed tube is used as a pipette, and permits the rapid introduction of the amalgam

breaking off of the platinum wire at the point where it enters the glass.

The Committee is indebted to Dr. Hulett for many suggestions in the preparation of these Specifications.

Committee—

- H. S. CARHART, Chairman.
- G. A. HAMILTON.
- E. B. ROSA.
- C. H. SHARP.
- B. J. ARNOLD, Ex-Officio.

Phosphorus.—R. Schenck.—The black substance resulting from the action of piperidine on solid phosphide of hydrogen has a slightly variable composition (presence of oxygen) when the reacting materials have not been dried with exceptional care. In the latter case we get a certain amount of $P_3H_2 \cdot C_3H_5N$. The ammoniacal salt previously obtained is $P_3H_2 \cdot NH_3$. Ammonia does not blacken P_3H_2 immediately in the cold; the reaction is slow, but it also takes place on heating. In the second portion of his paper the author shows that in the transformation of white phosphorus into the red variety, in the presence of PBr_3 , the reaction is unimolecular and not bimolecular, as has been believed up to the present.—*Berichte*, vol. xxxvi., p. 4202.

PRESENT PROBLEMS OF ORGANIC CHEMISTRY.*

By W. A. NOYES.

(Concluded from p. 215).

WE must admit, then, that we have, at present, no satisfactory theory of double and triple unions, and that we have here a problem which demands a large amount of further work before it is solved. When the solution is reached we shall probably gain a new insight into the perennial question of the structure of benzene, and our knowledge of tautomerism will cease to be, as it is at present, almost purely empirical. It is possible, perhaps probable, that Thiele's "conjugated double unions" will contribute toward the solution.

While I have no comprehensive theory with regard to double unions to advance, I will, with a good deal of hesitation, venture to express some thoughts with regard to the combination of atoms in general which have some bearing on this question. We are all familiar with Faraday's law, that if a current of electricity is passed through a number of cells filled with solutions of different electrolytes, and arranged in series, exactly equivalent amounts of the various components will be liberated at the electrodes in the successive cells. The beautiful experiments of Professor T. W. Richards have demonstrated that we are dealing here with a law which is true for different solvents and over a wide range of temperature; and also that the law is true with a degree of absolute accuracy which is of the same order as the laws of the combination of elements by weight. We are compelled, then, to believe that there is associated with each valence of an ion as it is transported through a solution, or at least as it separates at an electrode, a quantity of electricity which is invariable and independent of the nature of the ion. In other words, we have here a natural electrical unit which can be defined in its relation to atomic weights with a degree of accuracy which seems to be limited only by the refinement of our manipulations.

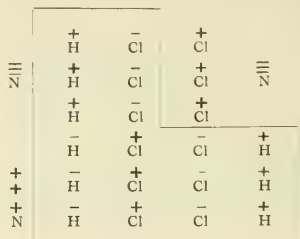
It is not always recognised as clearly as it should be that this unit quantity of electricity which is associated with one valence of any ion is not a unit of electrical energy. If it were, the same energy would be required to decompose the equivalent quantity of one electrolyte as of every other, which is manifestly not true. While the same current causes the separation of equivalent quantities in the different cells, the differences of potential, and so the amounts of energy required for the separation, vary greatly. It is evident then that when we say that a unit quantity of electricity is associated with each valence of every ion, we do not use the term *quantity* in the sense of quantity of electrical energy. Instead of this, when this conception of a unit quantity of electricity is examined, it will be seen that it is a conception of something whose properties are those of matter rather than those of energy. The facts appear to be consistent with the idea that the unit quantity of electricity of which we are speaking is of a material nature, and you have doubtless already perceived that I have the theory of electrons in mind. The ingenious experiments of J. J. Thompson have given us considerable reason for thinking that the negative electrons are capable of an independent existence, and have also given a probable estimate of their mass, which is small in comparison with the mass of the hydrogen atom.

It has been customary to think of the unit charge of electricity as being involved only in those reactions which occur in solution. If, however, we accept the theory of electrons it is evident that the electrons must be present in the molecule of an electrolyte no matter in what manner it is formed. It is but a step further to the conclusion that the electrons are involved in every combination or separation

of atoms, and, indeed, may be the chief factor in chemical combination.

Professor Kahlenberg has shown that a practically instantaneous reaction takes place between hydrochloric acid and copper oleate in a solution in dry benzene (*Journ. Phys. Chem.*, vi., 1), although the solution does not conduct an electric current, and there is no evidence of the dissociation of either the copper oleate or of the hydrochloric acid. Professor Kahlenberg points out very justly that there is no apparent difference between these reactions and those which take place in aqueous solutions, where we have much independent evidence of the existence of ions. He draws the conclusion that no ions exist in either case. It would seem that we are equally justified in supposing that a substance not already in the form of ions may separate into them under the influence of a second substance with which it can react.

Some time ago Mr. Lyon and myself (*Journ. Am. Chem. Soc.*, xxiii., 460) showed that the primary reaction between chlorine and ammonia gives nitrogen trichloride, nitrogen, and hydrochloric acid, and that these products are formed in such proportion as to lead to the conclusion that three molecules of ammonia react simultaneously with six molecules of chlorine. It was pointed out at the time that the simplest explanation of this result is to be found in supposing that chlorine atoms separate during the reaction into positive and negative ions, while the ammonia separates partly into positive nitrogen and negative hydrogen, and partly into negative nitrogen and positive hydrogen. This was represented graphically thus:—



This hypothesis has met with some approval (Stuglitz, *Journ. Am. Chem. Soc.*, xxiii., 797), but has also received the criticism that such a dissociation as is supposed would result in the spontaneous decomposition of ammonia into nitrogen and hydrogen (*Zeit. Phys. Chem.*, xii., 378). This criticism loses its force if we suppose that the separation into ions takes place only under the immediate influence of the chlorine with which the ammonia reacts. It has been pointed out by many different authors (see Erlenmeyer, jun., *Liebig's Ann. Chem.*, cccxvi., 50) that a separation of atoms from each other must occur either before or at the same time that they enter into combination with other atoms. The only part essentially new in the hypothesis proposed is that this separation is into positive and negative parts, and that the same atom may be sometimes positive and sometimes negative. The idea of a dissociation which occurs under the influence of a reacting substance appears to be implied in a part of Professor Nef's discussion of methylene dissociation, but it is not always clear whether he has in mind chiefly a dissociation of this sort or one which is independent of the interaction of different compounds.

The thought that the same atom may be at one time positive and at another time negative is related to the older electro-chemical theory which supposed water to be positive in acids and negative in bases.

We assume, then, that in every reaction

* Read at the International Congress of Arts and Science in St. Louis, September 21, 1904. From *Science*.

each union involves an attraction between the positive and negative electrons which are associated with the two atoms that unite. In saying this I do not lose sight of the fact that such a thing as attraction *per se* in the sense that one body can influence another at a distance without an intervening medium, is, apparently, inconceivable. I think of the attraction as probably caused by some motion of the electrons which enables them to act on each other through the aid of the ether. It is convenient, however, to speak of this effect as an attraction, since our conception of its real nature is of necessity very vague. One advantage of the idea that the attraction of the electrons is of a kinetic nature is that we may conceive of the same electron as becoming positive or negative according to the nature of its motion.

The common conception at present is that an atom which has lost an electron becomes positive, while either the electron in its independent existence or the atom to which it is attached becomes negative. So far as I am aware, it has not been pointed out that this view leads to the conclusion that the same atom must, under different conditions, have a different weight. Thus a bivalent copper atom which has lost two electrons must weigh less than a univalent copper atom which has lost only a single electron. It is true that our methods of determining atomic weights are scarcely accurate enough to detect differences of this order. The suggestion which is made is that the electrons of two atoms which are united, have motions which correspond to positive and negative charges respectively, and that when the atoms separate these motions may be retained, or lost, as in the case of a mercury atom which is uncombined, or that the motions may be reversed. In accordance with the hypothesis outlined above we must assume that when two atoms separate either one may become positive; dependent partly on their nature, partly on the nature of the reacting substance. The conception here proposed is that of something very similar to the action of the pole of a magnet, which may attract another pole of the opposite kind, or induce the formation of a pole of the opposite kind, or it may reverse the polarity of another magnet.

(This is, of course, only an analogy, and must not be pressed too far; just as the electrical changes of atoms or ions conduct themselves very differently from those of masses. The latter divide themselves between two bodies in contact; the former may be transferred *completely* from one ion to another).

This is, perhaps, simpler than to suppose the transfer of an electron from one atom to another in those cases where the electrical charges of the atoms are reversed in the ionisation. A very accurate determination of the atomic weight of cupric copper as compared with that of cuprous copper might possibly decide between the two hypotheses.

It should be noted that the hypothesis that the electrical charges associated with the atoms are of a kinetic nature, and that these charges may be transferred without gain or loss of matter, is quite independent of the first hypothesis, which is that the atoms are ionised when they separate from each other, and that the same atom may become either positive or negative.

In following farther the thought of the attraction between electrons as the cause of chemical combination, we must suppose that in addition to the effect of this attraction in holding together the atoms which are immediately attached there is a residual effect upon other atoms within the molecule. This gives a rational explanation of the very great difference in the stability of the union between carbon atoms in different compounds, as, for instance, the instability of acetic acid in comparison with butyric acid, occasioned by the substitution of an oxygen atom for two hydrogen atoms of the latter. The study of organic compounds has given us a knowledge of a large number of cases of this sort, and our text-books contain many empirical rules about them, but there have been few, if

any, attempts to give for such facts any rational explanation.

In considering double unions three explanations suggest themselves:—1. We may suppose with Pfeiffer that such unions are in reality single unions and free valences. In this case the presence in adjacent carbon atoms of positive and negative electrons, which are uncombined, would reduce the attraction of each for the electrons of another molecule, thus explaining why two free valences are so much less active than a single one. 2. We may suppose that the carbon atoms are in reality doubly united, but that owing to the localisation of the electrons in definite parts of the carbon atoms, the four electrons involved cannot approach as near to each other as is the case in a single union. This is Baeyer's theory of strain, and is much better in accord than is the theory of free valences, with the fact that cyclopropane and propylene appear to be about equally unsaturated, as evidenced by their heats of combustion and by their conduct toward bromine. On the other hand, it seems to lead logically to conclusions with regard to the addition of bromine to triple unions which Professor Michael has shown are contrary to the facts. 3. Without a condition of strain, we may suppose that the presence of both a positive and negative electron in each of the atoms united by the double union causes a lessening of the attraction of the electrons. This would result in such a union being less stable than a single union. The second and third views appear at present most in accord with the facts—possibly the truth lies in some combination of the two.

Whatever view we may take, it is noteworthy that double unions are usually formed by the loss of a positive and negative atom or group from adjacent carbon atoms, as hydrogen and hydroxyl or hydrogen and bromine. It is also true that in many double unions one of the carbon atoms is more positive than the other, causing the addition of halogen acids in a definite manner which may be predicted in accordance with Michael's "positive negative law." Applying this thought to conjugated double unions we see that of the four atoms involved the two central ones are likely to be positive and negative respectively, and neutralise each other's attraction for outside atoms, while an intensified attraction for outside atoms would be found in the exterior atoms. The effect may be analogous to that of the attractive forces of a magnet which exhibit themselves chiefly at the ends.

But I have permitted myself to wander much further in the field of speculation than was my first intention—further than is at all profitable, I fear, for these questions furnish at present few points for experimental study, and speculations divorced from experiment have usually been profitless. I should be very sorry if what has been said should give encouragement to such speculations. On the other hand, I have a very firm conviction that we should not be content with rounding out organic chemistry as a descriptive science, nor even with adding to the number of empirical rules which enable us to predict certain classes of phenomena. We must, instead, place before ourselves the much higher ideal of gaining a clear insight into the nature of atoms and molecules, and of the forces or motions which are the real reason for the phenomena which we study. When we consider the progress which has been made and the knowledge of structure we now possess, which would have appeared sixty years ago to lie beyond the limits of possible acquirement, it is not presumptuous to think that a more complete knowledge of these questions will at some time be gained. This fuller knowledge will take account, too, of many lines of work upon which I have no time to dwell, such as the question of changing atomic volume to which Professor Richards and Traube have directed our attention, and the knowledge of heats of combustion, of molecular refraction and dispersion, of colour, viscosity, dielectric constants, and other physical properties. The future must give to us a new theory or a development of old ones which shall include all of these phenomena in one comprehensive view.

A RADICALLY NEW METHOD FOR THE DETERMINATION OF SULPHUR IN IRONS AND STEELS.*

By H. B. PULSIFER.

It is with some hesitation one proposes a new method for a determination so long and ably carried on as the determination of sulphur in irons and steels. However, it must be admitted that the two methods at present recognised as giving accurate results, namely the nitric acid method and Bamber's method, are by no means ideal.

These methods are too well known to require description here; Ford and Willey have ably criticised them in a recent article in the *Journal of the American Chemical Society*. The author heartily shares their opinion that for accurate results with the nitric acid method great care is necessary.

Although these methods may be accurate when solution takes place slowly, because of this necessary slowness they lose their commercial value. An ideal method is one which should not lose accuracy when conducted by a skilful but rapid manipulator. Hastening the solution of the iron when dissolved in nitric acid does give low results, while if one resorts to evaporation on a hot plate there is much danger of losing sulphur by bumpings. To devote three-quarters of an hour to the solution alone makes this a very tedious method indeed.

In view of these facts, the author devised and tried the method which will be found below. The time between weighing the sample and precipitating the barium sulphate need not be more than twenty minutes.

Outlined, the process is as follows:—The sample is dissolved in chloric, hydrofluoric, and hydrochloric acids; the residue is then filtered, fused with sodium peroxide, and the fusion dissolved in water and hydrochloric acid. Meanwhile the hydrofluoric acid from the first filtrate has been boiled off, and the two portions are now united and the sulphur precipitated as barium sulphate.

Every step, excepting the boiling off of the hydrofluoric acid, is susceptible of quick and easy manipulation. The solution requires not over two minutes, while the fusion and its dissolving takes less than five minutes. As a matter of fact, several of the results given below took just under twenty minutes between weighing and precipitating.

Hendrixon (*Journ. Am. Chem. Soc.*, xxvi., 747) has shown that iron is quickly and completely dissolved by chloric acid, and that every trace goes to the ferric condition. This also oxidises the sulphur, as the results show. The residue, however, retains some of the sulphur, and its separation from the solution by suction filtration without removing the silica is an endless task, hence the use of hydrofluoric acid. A shorter method for this step would be highly desirable, but even as it is, it is not too tedious, and it unquestionably greatly assists in the rapid solution of the iron, its freeing the iron from silica giving the chloric acid full play on the iron.

The fusion of the residue with sodium peroxide is a very neat and easily performed operation. Once, while putting the sodium peroxide into the crucible on top of the folded moist filter containing the residue—the crucible having just been removed from the flame where it had been drying—sufficient heat remained to ignite the mass, and the whole fusion was completed in five seconds. It is also a pleasure to dissolve and filter a peroxide fusion, as it does not require that patience-trying deliberation needed for the solution and filtration of a sodium carbonate fusion.

The exact details by which the following results were obtained will now be given:—

Two and five-tenths grms. of the sample are placed in a 250 c.c. broad Jena beaker and just fairly moistened with water. The particles inevitably tend to fuse together if chloric acid is put directly on the iron, and the mass is then difficult to get into solution.

Twenty c.c. chloric acid (1·12 sp. gr.) are added and a very little hydrofluoric acid. In fifteen seconds the bubbles are at the top of the beaker, but have never been known to go over. In forty-five seconds the action has subsided, and 5 c.c. of strong hydrochloric acid may be added, the beaker covered with a watch-glass, and any particles on the sides brought down by boiling. It might appear feasible to boil off the excess of hydrofluoric acid at this point, but it was found that this always gave low results.

The filtration is now made by suction, using a 7 c.m. filter. The filter is washed two or three times with as little water as possible and then sucked as dry as may be.

To the filtrate 20 c.c. of strong hydrochloric acid are added, and the whole boiled down over a naked flame, with constant shaking, until the volume is under 10 c.c. and the mass begins to get oily; it is then placed on one side until the portion from the residue is ready to add.

Meanwhile the residue has been placed in a 20 c.c. nickel crucible and covered with sodium peroxide; the cover is then held down by the tongs while a strong flame heats the crucible. The action begins with a little pop and in a few seconds it is over. As soon as the fusion is solid it is cautiously placed in a beaker containing 50 c.c. of water. Hydrochloric acid is added, and in some two minutes all has dissolved, and the few shreds of unburned carbon may be filtered off, while the filtrate goes into the main portion already prepared and waiting.

The whole volume is now about 100 c.c., and is ready for the barium chloride solution.

The sulphur was determined separately in the two portions in the following analyses, so that the amount in the residue might be known.

Treadwell says that the presence of ammonium salts prevents the precipitation of barium fluoride, but this is very questionable indeed, and not confirmed by the author's experiments.

Of course, all the reagents used were tested for sulphuric acid. In portions as large as used for analysis none of them gave even a turbidity with barium chloride. Blanks were also carried through to prove that the hydrofluoric acid had been all removed by boiling as described.

No. 1.—A No. 1 Foundry Iron, Si = 2·97 per cent:—

Sulphur by usual rapid method.. 0·008 per cent
Sulphur by very slow solution .. 0·013 "

Sulphur by new method:—

Filtrate 0·012 per cent
Residue 0·006 "

Total 0·018 "

No. 2.—A No. 2 Foundry Iron, Si = 2·00 per cent:—

Sulphur by usual rapid method.. 0·004 per cent
Sulphur by very slow solution .. 0·003 "

Sulphur by new method:—

Filtrate 0·022 per cent
Residue 0·000 "

Total 0·022 "

No. 3.—A Steel, total carbon = 1·18 per cent:—

Sulphur by usual rapid method.. 0·017 per cent
Sulphur by very slow solution .. 0·023 "

Sulphur by new method:—

Filtrate 0·016 per cent
Residue 0·011 "

Total 0·027 "

No. 4.—A No. 1 Foundry Iron, Si = 2·84 per cent:—

Sulphur by usual rapid method.. 0·017 per cent
Sulphur by very slow solution .. 0·019 "

Sulphur by new method:—

Filtrate 0·026 per cent
Residue 0·020 "

Total 0·046 "

* From the Iron and Steel Magazine.

No. 5.—Also a No. 1 Foundry Iron, Si = 2.80 per cent:—

Sulphur by usual rapid method..	0.048 per cent
Sulphur by very slow solution ..	0.065 "
Sulphur by new method:—	
Filtrate	0.054 per cent
Residue	0.008 "
Total	0.062 "

No. 6.—A very soft Cast-iron, Si = 2.60 per cent:—

Sulphur by usual rapid method..	0.080 per cent
Sulphur by very slow solution ..	0.091 "
Sulphur by new method:—	
Filtrate	0.076 per cent
Residue	0.022 "
Total	0.098 "

No. 7.—A very hard Cast-iron, Si = 2.70 per cent:—

Sulphur by usual rapid method..	0.148 per cent
Sulphur by very slow solution ..	0.164 "
Sulphur by new method:—	
Filtrate	0.134 per cent
Residue	0.021 "
Total	0.155 "

The rapid method referred to is the standard method of solution in strong nitric acid and addition of strong hydrochloric acid when the first action of the nitric acid has ceased. It takes twenty minutes and gives low results.

The very slow method referred to is the same method exactly, except that the solution is made so slowly that at no time do nitric fumes come off rapidly. Solution takes at least thirty minutes, evaporations fifteen more.

Sample No. 3 was a steel in two small pieces, and by all methods took much more time than the samples in the form of drillings.

At the present time chloric acid is a rather expensive chemical for commercial work; however, it will probably be sufficiently cheap if there be much demand for it. Even at its present price it is not too dear, and if the accuracy of the method be sustained it may become the most desirable method after all. The acid with sp. gr. 1.12 is the only one readily obtainable; stronger acids might so reduce the amount of sulphur left in the residue that a fusion would not be necessary, which would greatly add to the desirability of the method.

The method is proposed for routine analysis in all sorts of laboratories, and if it does not come into general use it can at least serve as an independent check method for other methods.

Laboratory of the Henry Soutner Engineering Co.,
Hartford, Conn., August 19, 1904.

Tetraiodide of Zirconium.—A. Stahler and B. Denk.

—The authors heated zirconium, or pure carbide of zirconium, in a current of perfectly pure, dry hydriodic acid gas. Towards 340°, in the first case, and 490°, in the second case, a lively reaction took place, and a reddish sublimate was formed which was found to contain crystals of free iodine. To get rid of this iodine the sublimate was heated in a sealed tube with benzene to 100° with constant agitation. Finally they obtained a reddish-brown crystalline powder, fuming strongly in the air, reacting energetically on water and on the acids, and even with alcohol, forming ZrO_2 and C_2H_5I . It is slightly soluble in C_6H_6 and CS_2 , but more soluble in ether, giving a yellow colouration. The aqueous solution gives, on the careful evaporation of the oxyiodide, $ZrO_2 \cdot 5H_2O$, beautiful, colourless, very hygroscopic crystals, extremely soluble in water or alcohol. They are also obtained by the solution of $Zr(OH)_4$ in an aqueous solution of hydriodic acid. They correspond to the chloride and the oxybromide.—*Berichte*, vol. xxxvii., p. 1135.

PROCEEDINGS OF SOCIETIES.

THE FARADAY SOCIETY.

THE Eighth Ordinary Meeting of the Faraday Society was held on Tuesday, October 25, 1904, in the Library of the Institution of Electrical Engineers. Dr. F. MOLLWO PERKIN, Treasurer, occupied the chair.

Dr. HENRY J. S. SAND read an abstract of his Paper entitled, "The Measurement of the Potential of the Electrode in Stationary Liquids. The Determination of Changes of Concentration at the Cathode during Electrolysis."

The paper was illustrated by lantern views of the apparatus and of the curves embodying the numerical results of the author's experiments.

With a view to determine electrode-potentials in solution, the concentration of which in contact with the electrode should be known as accurately as possible, a method was elaborated for the measurement of potentials of electrodes in stationary liquids free from convection currents.

The apparatus employed was designed so as to allow the electrode to be placed accurately horizontally at the top or at the bottom, according as the electrolyte becomes lighter or heavier during electrolysis. The liquid connection to the normal electrode is tapped off about 3 to 4 m.m. in front of the electrode, the resistance between the junction and the electrode being found either by calculation or else directly by means of a Wheatstone-bridge arrangement for alternating currents, partly composed of condensers instead of resistances.

The method was checked by a series of experiments with a copper-sulphate solution, and gave satisfactory results for the diffusion coefficient of copper sulphate. The electrode-potential of a silver solution showed irregularities which are undergoing further investigation.

When two reactions take place, the method may show their successive occurrence by a sharp break in the potential-time curve, analogous to Nernst and Glaser's breaks ("knickpunkte") in their potential-current curves; the conditions existing at the electrodes are, however, more definitely known than in the "knickpunkt" method. An alcoholic solution of cuprous chloride which had become partially oxidised to cupric chloride showed such a break corresponding to the processes, reduction of cupric chloride and deposition of copper.

When acid solutions of nitrobenzene were electrolysed the time-potential curves showed characteristic retrogressions of potential after a definite time, possibly corresponding to changes in the condition of the cathode.

From experiments on alkaline solutions of nitrobenzene a lower limit for the diffusion coefficient of nitrobenzene in the solutions experimented upon was calculated, and it was shown that Haber's results regarding the dependence of electrode-potential or current-density cannot be explained by concentration changes at the electrode.

Dr. F. M. PERKIN referred to the great practical importance of potential measurements; for example, in oxidation or reduction processes slight differences in the potential often meant very great differences in the amount of energy absorbed.

Prof. THRELFALL said that there was too much uncertainty, due to unknown changes, in complex phenomena, such as had been investigated by the author for the experiments to yield a definite and finite answer. More valuable results might be looked for at the present stage of knowledge if the simpler problems in electrolysis—familiar difficulties that occur in one's daily practice—were attacked. As regards the experiments themselves, he thought that the method of employing a capillary tube in connection with the cathode for measuring electrode-potentials, would yield as accurate results as those obtained by the author.

Dr. SAND, in reply, said the chief purpose of his work

was to show the applicability and limits of his method, although he felt the force of what Professor Threlfall had said. The capillary-tube method was useless in experiments like these, which were really diffusion experiments, as he particularly wished to avoid convection currents.

Miss BUENA POOL, B.Sc., then read a "Note on a Suggested New Source of Aluminium."

The geological data given in the paper have already been published in the *Geological Magazine* by Messrs. Holland and Warth, but the authoress thinks they are of sufficient importance to be specially brought in this form before the notice of British electro-chemists. The new source referred to in the title is India, thousands of square miles of the surface of which is covered with laterite deposits varying from a few feet to hundreds of feet in thickness. These laterites, of which four distinct classes are described in detail, are closely analogous to bauxite, the aluminium being present in the hydrated form. From specimen analyses which are quoted, it would appear that the high-level laterites in particular bear an obvious and striking resemblance to ordinary bauxite. The low-level laterites contain much free silica and clay. The conclusion of the paper is that these Indian bauxites have all the characteristics to render them commercially valuable; their pureness, ready accessibility, widespread occurrence at all elevations, and association with flowing water, pointing them out as an almost perfect source of aluminium.

Mr. W. MURRAY MORRISON said that gibbsite could not be used as a direct source of aluminium, without being first treated for alumina. He did not think that the Indian laterites were likely to be used in this country at present, as we had a plentiful supply of French bauxite to draw from, but of course they might, in time, be worked *in situ*. There was as yet no great demand for aluminium in India.

Dr. F. MOLLWO PERKIN gave a short account of the paper by himself and Mr. H. D. LAW, B.Sc., entitled "Electrolytic Oxidation of Hydrocarbons of the Benzene Series." Part I. *Hydrocarbons containing the Methyl Group.*

Owing to the more or less fragmentary style, and the incompleteness of the literature dealing with the electrolytic oxidation of organic substances, the authors have commenced a detailed study of the electrolytic oxidation of hydrocarbons of the aromatic series.

They find that when an emulsion of toluene and dilute sulphuric acid or caustic alkali is electrolysed the whole of the toluene is burnt up, but that when a mixture of acetone and toluene is electrolysed in the anode compartment of a cell, benzaldehyde is produced. Unless, however, a large excess of acetone is present, the yield of benzaldehyde is very small—even under the best conditions they were unable to obtain more than about 8 per cent of benzaldehyde. The conditions employed were 550 to 600 c.c. acetone, 50 grms. toluene, and 250 c.c. of dilute sulphuric acid. Beside benzaldehyde a small quantity of another product was produced which may be benzyl alcohol or a condensation product of the molecules of the toluene. They further oxidised ortho-, meta-, and para-xylene, and mesitylene and pseudocumene under similar conditions. In each case the corresponding mono-aldehyde was produced, with on occasion small quantities of the dialdehyde. Small quantities of a neutral product were also obtained, which are under examination. In no case was the corresponding acid produced. In the case of ortho- and para-xylene the yield of aldehyde was from 25 to 35 per cent. With the meta-xylene the yield was not above 10 per cent. Contrary to experience in ordinary chemical oxidations, the meta-xylene seems to show a greater tendency to be burnt up than the ortho- and para-xylenes.

With mesitylene and pseudocumene, the mono-aldehydes were also produced. With the latter substance, apparently a mixture of the three possible isomers. Further experiments are in progress, and the authors are also investigating hydrocarbons of the benzene series containing other

groups than the methyl group and hydrocarbons containing mixed groups.

Mr. FRANK SHEDDEN, in a written communication, suggested the use of a gas-tight cell, and determining the amount of carbon dioxide given off, to show the extent of any "burning" that might be taking place. Had the authors lowered the current density by increasing the anode surface?

Dr. PERKIN said that they had begun to make a study of the gases evolved. Their anodes were of platinum, so they had only used small ones. The chief difficulty they wished to overcome was the formation of tarry products owing to the concentration of H_2SO_4 in the anode chamber after a time. Neutralisation or withdrawal of solution were both out of the question.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxiv., No. 14, October 3, 1904.

Actinium.—A. Debiere.—Several years after the author's first publication on actinium, M. Giesel announced the existence of a radio-active substance which he called "Emanium." The striking analogy between the properties of this substance and those of actinium led the author to suppose that they might be identical. He therefore, in conjunction with M. Giesel and M. and Mme. Curie, made several comparative experiments upon the phenomena of phosphorescence produced by emanations from emanium and actinium, and obtained identical results for the two substances. Miss Brooks has also found the same number for the time constant for decrease of radio-activity produced by emanium as the author had previously given for actinium. Hence the two substances must be identical.

Properties and Constitution of Molybdenum Steels.

—Leon Guillet.—The molybdenum steels can be divided into two classes:—(1) Perlitic, (2) carbide, according to their microstructure. Experiments show that the presence of molybdenum has the same effect as the presence of tungsten upon the properties of steel, *i.e.*, it increases the tenacity, elasticity, and (in the case of perlitic steels) the resistance to crushing force. The carbide steels are extremely hard and are brittle. Four times as much molybdenum as tungsten is necessary to produce the same effect.

Thermo-chemical Comparison between Rosanilines and Leucanilines.—Jules Schmiden.—Experiments on the heats of neutralisation of the rosanilines and leucanilines have established the following facts:—1. About the same amount of heat is emitted when a triacid carbinol salt is formed from a carbinol, as when the corresponding triacid leuco-salt is formed from leucaniline. 2. The heat emitted when 3 molecules of acid react to form a coloured salt is always greater than that emitted in the formation of the corresponding carbinol or leuco-salt. Hence the instability of the carbinol salts, and their tendency to form coloured salts with the production of heat. 3. In the formation of the coloured salts more heat is emitted when the first molecule of acid reacts than when the two following molecules react, and this is more marked in the stronger bases, *e.g.*, heat produced during action of first molecule of acid to heat produced during action of second molecule = 3 : 1 in the case of rosaniline and = 6 : 1 in the case of hexamethyl rosaniline. These experiments confirm previous observations that the rosanilines, though triamines, behave like very strong monacid bases. This power of accumulating the basic properties in a single group seems to be connected with the quinone nucleus.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxvii., No. 13, 1904.

Action of Nitric Oxide on Chromous Salts.—V. Kohlschütter.—Three molecules of chromous chloride absorb from 1:2 to 0:87 molecules of nitric oxide, the colour of the solution changing to dark red. This was supposed to be due to the formation of the compound $(\text{CrCl}_2)_3\text{NO}$, which is very stable, absorbs no more oxygen, and does not give up NO on heating or *in vacuo*. But the author has found that this red solution gives only chromic reactions, and that nothing points to the presence in it of a NO group. Its colour slowly changes in the cold (rapidly on heating or on addition of acids) to a tint between olive-green and brownish red. The freshly prepared dark red solution was distilled with alkaline permanganate solution:—(1) Directly, and (2) after being previously warmed with hydrochloric acid, and the ammonia thus formed was determined by titration. Since alkaline permanganate decomposes hydroxylamine, if any of the latter compound were formed on acidulation the ammonia formed in the second case would be less in quantity than in the first. But it was found that the same amount of ammonia was formed in both cases. Hence, the colour change on addition of acid does not show the decomposition of a nitric oxide compound, but proves that ammonia and hydroxylamine are present in definite amounts in the red solution. Thus the absorption of nitric oxide by chromous chloride depends upon its reduction to soluble compounds—ammonia in neutral solutions or hydroxylamine in acid solutions. More chromous chloride is necessary to convert a given quantity of NO to ammonia than to hydroxylamine, and this agrees with the fact that the same chromous solution absorbs less NO in neutral than in acid solution. Nothing definite can be said regarding the nature of the red solution; perhaps it is a solution of a basic chromic salt which, like the sulphate or chloride, can pass into other hydrated forms.

Phosphorescing Zinc Sulphide.—H. Grüne.—Following Henry's directions for the preparation of zinc sulphide the author could get no uniform results in many experiments, obtaining preparations which sometimes gave stronger and often weaker phosphorescence. The more the zinc salt was purified the weaker was the blende obtained. The addition of traces of other metallic salts to the pure zinc salt gave strongly phosphorescing sulphides generally. Thus less than 1/1000 of copper gave a green phosphorescence; silver, lead, bismuth, tin, uranium, cadmium gave good preparations, while iron, nickel, cobalt, and chromium gave negative results. Manganese produced very characteristic effects. After illumination preparations of zinc sulphide containing traces of manganese phosphoresced with a reddish yellow light; rubbing or scratching caused an extraordinarily strong luminescence which could be seen even by daylight. When in the state of the finest powder the preparation phosphoresced under gentle pressure. Preparations containing other metals, *e.g.*, copper or uranium, showed this kind of phosphorescence, but to a much slighter extent.

Quantitative Determination of Active Oxygen in Organic Persulphates.—A. Wolf and R. Wolfenstein.—In inorganic persulphates the active oxygen is determined by heating a weighed amount of the persulphate with a solution of Mohr's salt and titrating the unoxidised part with *n/10* permanganate. This method cannot be used for organic persulphates, for even supposing the Mohr's salt is readily oxidised the excess cannot be titrated with permanganate on account of the presence of the organic substance. The following method depending on the oxidation of sulphurous to sulphuric acid by means of the persulphate was devised to obviate this difficulty:—A saturated aqueous solution of sulphurous acid, to which some barium chloride had been added, was filtered and heated in an Erlenmeyer flask with a weighed quantity of persulphate and some hydrochloric acid. On cooling the BaSO_4 formed was filtered off and weighed:

$\text{H}_2\text{S}_2\text{O}_8 + \text{SO}_2 + 2\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4$. In calculating the active oxygen it must be remembered that the available oxygen is only responsible for the formation of one-third of the total BaSO_4 obtained, as shown by the equation.

Action of Acid Dyes on Wool Fibres.—Edmund Knecht.—The elaboration of an accurate method of estimating azo dyes and certain nitro dyes has enabled the author to establish the fact that the so-called acid dyes are taken up in the proportion of their molecular weights when wools are coloured by them. Mixtures of the wool with 50, 25, &c., per cent of dye and 30 per cent sulphuric acid were heated for an hour. The amount of sulphuric acid was arbitrarily chosen, and seems to have no influence on the amount of dye taken up. Nor does the quantity of water employed seem to affect the amount of dye taken up by the fibre within fairly wide limits (50 to 200 times the weight of wool). This fact directly contradicts a solution theory. Moreover, the solubility of the dye in water does not influence the amount taken up. Five different classes of dyes were examined:—Orange G, Ponceau 2G, Orange II., Acid Magenta, and Picric Acid and its homologues, and in all cases they were taken up by the fibre in the proportion of their molecular weights. The sulphuric acid not only sets free the dye from its salt, but also acts upon the fibres so as to increase their power of taking up dye.

Luminescence of Sidot's Blende under the Influence of Ozone.—Rudolf Schenck and F. Mihr.—Certain analogies exist in the behaviour of ozone and of radio-active substances, *e.g.*, both form gaseous ions (if only to a slight extent in the case of ozone) on decomposition, which manifest themselves in the same way, *i.e.*, in the discharge of an electroscope and the vapour radiation phenomenon. Sidot's blende also becomes luminescent under the influence of ozone. The authors have previously found that the ozone converts the zinc sulphide into sulphate, and thus it is an oxidation luminescence similar to that of other oxidisable substances in ozone. They described the luminescence as nebulous, *i.e.*, a bright cloud seemed to extend over the blende in the current of ozone. On repeating the experiments under improved conditions they find that the phenomenon of scintillation is visible as well as the homogeneous luminescence of the preparation. Quite unused fresh blende, which had been carefully kept from any radio-active substances, was used for the experiments. Strips of paper prepared with this blende were kept in a closed cardboard box in the dark room for some time, then cut up in red light, and introduced into the apparatus. The authors first observed the blende preparations without passing the current of ozone through the apparatus, and without starting the inductor. In the first quarter of an hour, and generally the second too, nothing was to be seen, but gradually spots of light appeared flashing on all preparations, which became clearer. They could be seen either with a microscope or with the naked eye (a very short-sighted eye is best suited for this purpose). When unozonised oxygen was passed through the apparatus no alteration whatever occurred in the phenomena observed. The eye very soon becomes tired in observing this phenomenon, and must be rested to avoid errors in estimating the comparative brightness. Thus, Sidot's blende scintillates feebly without any radio-active substance. Soon after the inductor had been started for the production of ozone it was seen that the number of spots of light increased, and the intensity of the sparks also. The experiments were repeated, always with the same results. The authors found that feeble illumination, *e.g.*, with the help of a match, increases the scintillation. Thus it appears that all factors which cause Sidot's blende to luminesce homogeneously also excite the scintillation; an increase of scintillation does not necessarily show the presence of a radio-active substance and Sidot's blende is a reagent which must be used with great care. When frequently treated with ozone it no longer gives the homogeneous luminescence, but distinct scintillation can always be seen in such preparations.

THE CHEMICAL NEWS.

Vol. XC., No. 2346.

NOTE ON THE HIGHER GLYCERIDES.*

By J. B. HANNAY, F.R.S.E., F.I.C.

(Concluded from p. 225).

SEVERAL analyses of the lead compounds formed by treatment of the new compounds with water proved them to be basic salts of the formula—



where F represents the radical of the fatty acid.

A mean of four analyses of the dehydrated basic oleate and linoleate gave 41.68 per cent of lead for the oleate as against 41.73 required by theory, and 41.96 for the linoleate as against 41.87.

To ascertain if the basic oleate and linoleate so obtained could be formed directly, a weighed quantity of the acids was mixed with sufficient oxide of lead to form a normal salt, and the moisture evolved was weighed. 7.5415 grms. of oleic acid gave off 0.2540 H₂O. Theory requires 0.2406. Another molecular proportion of PbO was then added, and heat applied. When it was completely dissolved there had been evolved only 0.0070 grm. H₂O, showing that the second molecule is simply an additive compound to form the basic salt.

Similar results were obtained with linoleic acid, but the full quantity (or an excess) of oxide of lead was added at once, with the result that invariably only half the water represented by the litharge combined was evolved.

Mercury thymol acetate forms a double compound with mercury acetate, and it was attempted to ascertain if an analogous compound was formed between lead glyceryl oleate and lead acetate. As anhydrous lead acetate is insoluble in hydrocarbons, while the glyceryl compound is very soluble, an easy method was afforded of separating these substances. Molecular proportions of the two were fused together, and on cooling they formed a homogeneous mass, which was freely soluble in benzene, chloroform, &c., showing that no free lead acetate existed in the material. The solution was partially precipitated with absolute alcohol. The precipitated portion was collected and dried, and the part remaining in solution evaporated to dryness, and the two analysed.

The lead acetate contained	63.69	per cent Pb
The lead glyceryl oleate	39.99	"
The double compound should contain ..	44.08	"
The precipitate gave	44.21	"
The soluble portion	44.05	"

The result is high, but the acetate becomes basic when the water is driven off, and the mixture gave 44.06 per cent Pb, so that the fractional precipitation did not split up the compound, and this affords confirmation of the analogy with mercury thymol acetate.

The lead in the lead glyceryl oleate is not attacked by sulphur nor phosphorus in carbon disulphide, nor by phosphorus pentoxide, nor sulphur trioxide, nor is it displaced by fusing the compound with metallic sodium.

The lead glyceryl oleate and linoleate were digested with carefully dried absolute alcohol for periods up to two hours, but no trace of glycerin was extracted, showing that the ester had been in no way split up. Of course any water

in the alcohol at once completed the saponification of the oil, and the glycerin was set free.

Experiments were made to ascertain if hydrate of lead, or carbonate of lead, or any of their combinations known as Dutch white lead, can combine in the cold with triolein or trilinolein, and they have shown that no action takes place with any of these bodies, even if the mixture be kept (as has been done in these experiments) for a period of nine years.

Sodium carbonate reacts with oils, but at a very much higher temperature; carbon dioxide being freely evolved at 270° to 290°, and the oil much blackened. The resulting combination is a tough leathery body, quite unlike the lead compound. The sodium being monovalent, the reaction most probably forms tri-sodium glycerin and oleate of sodium, thus—



Action of Sulphur Chloride on Glycerides.

It was found, contrary to the indication of other experimenters, that under proper conditions the amount of sulphur chloride capable of combining with any oil was in the exact proportion required to saturate the free linkings of the acid radicals, and thus exactly parallel with the bromine or iodine absorption, taking S₂Cl₂ as divalent. To clear up the matter the iodine, bromine, sulphur chloride, and oxygen absorptions of pure oil and linsed oils were determined.

The oxygen absorption was conducted on thin silver trays with a surface of about 100 square centimetres, and the oil was spread in a layer of from 0.025 to 0.035 grm. per square centimetre, as it was found that thicker layers absorbed the oxygen more slowly, and their lower layers were protected from oxidation by the upper oxidised layers.

In 115 days at summer temperatures, from June till September, linsed and poppy oils had absorbed practically all the oxygen they were capable of fixing.

The olive oil was spread very thinly on lead, in an atmosphere saturated with moisture, as it showed no signs of drying on silver, and did not cease to gain weight, even at the end of three years' exposure on lead. Many conflicting statements and empirical experiments are to be found as to the action of sulphur chloride on oils. After some experimenting it was found that the causes of the differences lay in the use of various diluents, adding an insufficient quantity of the chloride, and in allowing the temperature to rise, which results in the chlorine of the sulphur chloride attaching itself to the glyceryl radical, and in forming substitution compounds with the hydrogen of the acid radical, giving rise to chlorhydrins and hydrogen chloride.

By cooling the materials in ice and keeping them cooled while mixing, they slowly form a jelly, and no by-products are formed.

The combination was prepared in two ways:—

1. By mixing the materials in molecular proportions; i.e., three of sulphur chloride to one of the triolein, and six of sulphur chloride to one of trilinolein.
2. By using an excess of sulphur chloride and placing the solid in a desiccator over sticks of caustic potash to absorb the excess of sulphur chloride.

The compounds formed by these methods were analysed by boiling with strong nitric acid in a Jena glass flask. About one-third of the chlorine comes over as nitrosyl chloride, and is retained by being passed into a solution of alkali, while the sulphur, which attached itself to the acid radical, forms a sulphonic acid. This is rendered alkaline by sodium carbonate, a little nitre added to ensure excess of oxidising agent, and the whole evaporated to dryness, and fused in the same flask, and the chlorine and sulphur estimated as silver chloride and barium sulphate.

The substance prepared as above gave:—

* The substance of a Paper read before the Chemical Society.

	Found.		Theory.	
	S.	Cl.	S.	Cl.
For the olein compound..	14.04	15.47	14.89	16.52
For the linolein compound	21.42	23.21	22.74	25.23

When prepared and left at ordinary temperatures fumes were given off, and the composition was :—

Linolein compound..	S = 24.92	Cl = 19.17
Boiled with CS ₂ and filtered it was further decomposed ..	S = 21.45	Cl = 13.29

Showing that sulphur was comparatively firmly fixed, while the chlorine was driven off.

To make these results comparable, the olein has been taken as having six free bonds (absorbing 6 of Br), and the linolein as having twelve, although both oils usually contain from 5 to 10 per cent of other oils—stearin and palmitin in olive oil, and olein in the linseed oil, which lower the saturation equivalent. The following shows that the compounds formed by iodine, bromine, oxygen, and sulphur chloride are all formed by the saturation of the same free linkages, as shown by the structural formula on p. 224 :—

Olein taken.	Saturated by—	Per cent.	Theory.	Percentage of theoretical.
2.1725	Iodine 1.7923	82.5	86.2	95.7
2.2650	Bromine 1.1800	52.1	54.3	95.9
1.8273	Oxygen 0.0895	4.9	5.4	90.2*
13.2725	Sulphur chloride 5.7735	43.5	45.8	94.9

Linolein taken.

2.0840	Iodine 3.2593	156.4	174	89.8
3.6615	Bromine 3.6254	99.1	109.3	90.9
1.8580	Oxygen 0.1801	9.69	10.9	88.9*
2.5205	Sulphur chloride 2.1065	83.5	92.3	90.4

* Action not complete.

From these figures it is clear that the sulphur chloride and oxygen saturation numbers are caused by the combination with the same unsaturated linkages as combine with the iodine or bromine. One would expect it to be so, but as much mystery surrounds the sulphur chloride compound in most of the published researches, it was thought worth while to make an exact examination. The numbers quoted are taken out of many trials conducted over several years.

It was found that the lead glyceryl compounds described in the first part of this paper were capable of forming the insoluble sulphur chloride combination, but it was less stable than that with the free oil, so the point of saturation was determined by the failure of the sulphur chloride to produce any further precipitate in a solution of the lead glyceryl compound in a hydrocarbon solution. The bromine saturation numbers were determined at the same time.

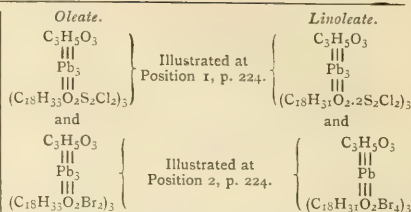
Lead glyceryl oleate taken.		Per cent.	Theory.	Per cent of theoretical.
2.7590	Bromine	0.7863	28.51	30.91
3.0050	S ₂ Cl ₂ ..	0.7150	23.8	26.01
				91.5

Lead glyceryl linoleate taken.					
2.1115	Bromine	1.1782	55.8	62.05	90.0
2.6040	S ₂ Cl ₂ ..	1.2265	47.1	52.3	90.1

These numbers show that here again we have a close approximation to the theoretical figures, showing that the same bonds are active in the lead compound, as in the original oil.

The saturation of the free linkages of the acid radicle by oxygen gives a solid compound in the case of both oleic and linoleic glycerides; the latter forming "linolein," the solid pellicle familiar in paints, and having the composition C₅₇H₉₈O₁₂, the oil taking up 6 of oxygen to saturate the free linkages, as at Position 3, p. 224.

The lead glyceryl oleate and linoleate compounds with bromine and sulphur chloride may be represented thus :—



It seemed strange that, during these researches, carried out over a period of nine years, in all the samples of linseed and poppy oils, and the acids prepared from them, there never was the slightest indication of Hazura's linolenic and isolinolenic acids, supposed to have an iodine absorption power showing six linkings, *i.e.*, eighteen free bonds in the triglyceride. In every case the iodine absorption has been a little below that due to linoleic glyceride, *i.e.*, twelve free linkages, the deficiency being due to oleic and perhaps traces of palmitic glycerides.

Hazura gives the composition of the acids from the glyceride called linseed oil as :—

	Per cent.	Iodine absorption.	
		As glycerides.	As free acids.
Linoleic acid ..	15	26	27
Linolenic acid ..	15	39	41
Isolinolenic acid ..	65	170	178
Saturated acid ..	5	0	0
	100	235	246

Now the highest absorption for linseed oil or the acids directly derived from it by any experimenter is 160, and Hazura himself gives 156, a value quite inconsistent with the existence of linolenic and isolinolenic acids, while the theoretical number for pure triolein is 174, so that Hazura's number shows a deficiency of about 8 per cent due to impurities, and agreeing well with all my figures before given. In these investigations over 200 samples of pure linseed oil have been brominated or saturated by Hübl's method with iodine, and not one gave an iodine number over 160; and over forty samples have been saponified, and the acid or acids saturated with bromine or iodine, but in no case was a higher iodine number than 166 obtained (or 100 in the case of bromine), which are again well under the numbers (181 and 114) for the absorption numbers of linoleic acid.

As Hazura gave an iodine number for linseed oil (156) agreeing with all other investigators, and well under the number for an acid with four free linkages, and yet found acids (after hydrolysis and reduction of those obtained from the same oil), which showed iodine numbers indicating acids with 6 free linkages, an investigation into the real meaning of Hazura's numbers seemed imperative, as I had been unable to find any trace of these highly unsaturated acids by any means of saponification, alcoholic or otherwise, which I had tried.

Suspecting that the acids obtained by Hazura from the alkaline permanganate treatment were products of decomposition of the linoleic acid from over oxidation, a series of experiments were instituted, under which the acids from linseed oil were exposed to the action of alkaline permanganate varying in three directions, *viz.*, time, concentration, and temperature.

The method was to make the mixture, allow to stand a given time, then dilute to the same volume in every case, and reduce or raise the temperature to 16°, then filter off the oxy acid formed, and dry it in a desiccator, and weigh it.

It was soon apparent that great dilution of the acid soap led to the oxidising action going too far; in fact, beyond

the mere saturation (or hydrolysis) of the oxy-acid, and that it struck more deeply and formed acids of the azelaic type, and the yield of oxystearic acid was diminished. A rise of temperature led to the same result, as did large excess of permanganate and a longer time; but the insoluble acid obtained never showed a higher acetyl value, determined by Lewkowitsch's method, than corresponded to the tetra-oxystearic acid. The greatest yield of the oxy-acids, which sometimes reached 92 per cent of the theoretical, was obtained by treating the acid soap with a rather concentrated solution of the permanganate (about 4 per cent giving good results) and allowing it to stand with an excess at 0°, when a good yield is obtained. Hazura's method of isolating the isolinolenic acid by brominating the acids in acetic acid solution yields very complex results (substitution products being formed, and a large excess of bromine being required), but if brominated carefully in chloroform, taking care to add a very slight excess of bromine, the bromo derivative, on being reduced by zinc and acid, yields only the original linoleic acid with an iodine value of 170 or under, according to the purity of the original oil used.

These experiments have been repeated with poppy oil and hemp-seed oil with similar results—no acid with a higher value than I_4 was formed—and this agrees with the results of Reformatzky (*Ann. Russ. Chem. Soc.*, xxi., 202) who found that pure linoleic acid, prepared from its ethyl salt, gave only a hydroxy acid of $(OH)_4$, and no linolenic or isolinolenic acids; but that permanganate oxidation at ordinary temperatures always produced some products of deep oxidation, as azelaic and formic acids.

Hence the conclusion is that in natural vegetable oils the highest iodine value is one of I_4 in linoleic acid, and that the linolenic and isolinolenic acids, if they exist, are products derived from linoleic acid by the replacement of some of the hydrogen of some members of the methane chain, by hydroxyl derived from the oxygen of the permanganate.

A MODIFIED FORM OF THE PERSULPHATE METHOD OF ESTIMATING MANGANESE IN IRON AND STEEL.

By H. PROCTER SMITH, F.C.S.

The estimation of manganese in iron and steel may be performed in many different ways, but in the author's opinion, for accuracy, speed, cleanliness, and cost, nothing beats the persulphate method.

The following modification gives most satisfactory results, and may be used for all classes of iron and steel:—Weigh into a 6" x 1" test-tube 0.2 gm. of the sample and the same weight of a steel, the amount of manganese in which has been previously determined by a gravimetric method; add from a burette 10 c.c. nitric acid (1.2) to each, and dissolve by heating over a small flame; boil until all red fumes are driven out of the tube, then add 10 c.c. of the silver nitrate solution, and about 1 gm. of solid ammonium persulphate dropped into the solution by means of a spatula; warm gently over flame until the salt is nearly dissolved; then wash any salt remaining on the sides of the tube down, and place in a bath of cold water. When perfectly cold the pink solution is washed into a clean porcelain dish, and titrated with the standard solution of sodium arsenite until one drop turns the solution from a pinkish tinge to a very pale green. The strength of the arsenite is determined each time by means of the standard manganese steel, and thus a factor obtained; e.g., a steel containing 0.45 per cent of manganese took 4.3 c.c. of arsenite, then $0.45 \div 4.3 = 0.105$. Then number of c.c. of arsenite for any other steel multiplied by 0.105 = percentage of manganese in the steel.

The change from the pinkish colour to the green is most

marked, and cannot be missed by an operator, even when using the method for the first time. With pig-iron there is no need to filter off the graphite, as it does not interfere with the titration. Should a titration be overdone, it can easily be brought back to the original state by adding a further portion of ammonium persulphate and gently warming, when the pink colour is restored, and after cooling may be re-titrated.

Silver Nitrate Solution.—Pure silver nitrate, 1.70 grms.; distilled water, 1000.0 c.c. This is approximately a centinormal solution.

Sodium Arsenite Solution (stock).—Pure arsenious acid, 5 grms.; pure bicarbonate of soda, 15 grms. Dissolved by boiling in 250 c.c. water, and diluted to 1000 c.c. when cool.

For use:—40 c.c. of above diluted to $\frac{1}{2}$ litre, when 1 c.c. = approximately 0.1 per cent manganese.

The following comparative results taken at random from the author's note-books confirms the accuracy of the method:—

	Gravimetric method. H ₂ O, %.	Gravimetric method. Mn per cent.	Ford and Williams HNO ₃ + KClO ₄ Mn per cent.	Lead peroxide. Com- parison of colour. Mn per cent.	Ammonium persul- phate. Titration with arsenite. Mn per cent.
Cast H 1241 ..	0.53	0.52	0.525	0.52	0.52
" A 241 ..	0.61	0.61	0.60	0.615	0.615
" B 24 ..	0.45	0.455	0.42	0.445	0.445
Blow 249 ..	0.89	0.86	0.87	0.875	0.875
KB3 ..	0.19	—	0.18	0.185	0.185
Scotch hematite	1.66	1.59	—	1.63	1.63
"	1.30	1.21	—	1.30	1.30
Bar iron ..	0.129	—	—	0.11	0.11

This process can easily be worked to give the manganese contents in any steel in under fifteen minutes from commencing to weigh out the sample, and hence is particularly useful where the manganese is required before tapping a basic open-heat where manganese ore has been used in "feeding."

Shotton, Flint.

VOLUMETRIC ESTIMATION OF VANADIUM AND CHROMIUM IN SOLUTION TOGETHER.

By EM. CAMPAGNE.

THE quantitative separation of vanadium and chromium is very difficult on account of the numerous properties common to both of these elements. The methods of estimation proposed up to the present have been recently the subject of a paper by M. Nicolardot, who has recommended a method based on the separation of the chromium in the form of the very volatile chloride of chromyl.

All these old methods have the drawback of requiring an effective separation of the two elements before coming to the estimation proper. This separation can only be effected after long and delicate manipulations, so that methods based on this principle do not seem to us to answer to the requirements of analyses for commercial laboratories.

A consideration of certain known reactions has led us to devise a method for the volumetric estimation of these metals, which has the advantage of not requiring their previous separation, and of being applicable even in the presence of small quantities of other metals.

Further, this method of estimation is closely connected with the method of estimating vanadium we have described recently (*Comptes Rendus*, 1903, vol. cxxxviii., p. 570); it can be applied to the vanadiferous minerals and to ferro-metallic alloys.

To detect chromium in the presence of vanadium, a few grms. of the mineral (or the oxides resulting from the careful calcination of the nitrates obtained by attacking the alloy with nitric acid) are fused with a mixture of nitrate and carbonate of soda in equal parts.

The mass is taken up with water; the metallic oxides, that of iron amongst others, remain insoluble, and the solution contains the vanadium and the chromium in the form of vanadate and chromate.

Acidulate with sulphuric acid, and take a few c.c. and shake in a test-tube with a little peroxide of hydrogen and ether. If the two metals are present the aqueous solution takes a blood-red colour (vanadium), and the etherial solution a very intense but fugitive blue (chromium). In the contrary case neither one nor the other of these reactions is observed.

Successive Estimation of Vanadium and Chromium.

If we have to do with a metallic alloy (ferrochromo-vanadium) we attack with nitric acid, gently calcine the nitrates to obtain the corresponding oxides, which are dissolved in concentrated hydrochloric acid. The proportion of iron generally being considerable, it is eliminated by Rothe's method (treatment of the chlorides by ether). As far as concerns the details of the attack and the method of procedure, we refer the reader to our previous paper already quoted.

The aqueous solution obtained by this treatment contains all the chromium and vanadium that was present in the alloy or mineral, besides small quantities of ferric chloride. This solution of chlorides is evaporated several times in the presence of a large quantity of concentrated hydrochloric acid, so as to bring the vanadium into the state of oxychloride, VOCl_2 , and the chromium into the state of chloride, Cr_2Cl_6 . If the original solution was a mixture of chromate and vanadate, the reduction should be conducted in exactly the same manner; for the reduction to be complete, it is important that the solution should not contain any free sulphuric acid.

After the reduction the solution is treated with 10 c.c. of pure sulphuric acid and evaporated on the sand-bath until white fumes begin to appear. Thus we obtain sulphate of chromium, $\text{Cr}_2(\text{SO}_4)_3$, and the blue divanadyl sulphate, $\text{V}_2\text{O}_2(\text{SO}_4)_2$.

The estimation of the vanadium is based on the fact that the divanadyl sulphate is oxidised rapidly, and in the cold by permanganate of potassium, while the sulphate of chromium remains perfectly stable under these conditions.

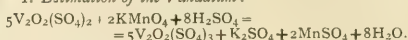
The cooled sulphuric solution is diluted with 250 c.c. of distilled water, and then titrated at the ordinary temperature with a solution of permanganate of potassium. The decoloration of the solution is rather slow at first, but can be hastened by stirring frequently. The oxidation of the salt of vanadyl is complete when the rose-colour of the KMnO_4 persists for several minutes in spite of the stirring, and when a drop or two of permanganate will make it reappear.

This titration completed, we add a large excess of permanganate (5 or 10 c.c. of a 1 per cent solution), and boil briskly so as to change the sulphate of chromium into chromic acid; the solution ought to remain rose-coloured on account of the excess of the oxidising reagent, an excess which is subsequently got rid of by the addition of a few pieces of filter-paper and further boiling. After cooling, the solution is filtered to separate the binoxide of manganese formed, and we obtain a solution of vanadate and chromate having the characteristic yellow colour of the latter salt.

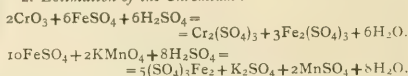
To this solution we add a known quantity of a solution of Mohr's salt, titrated with permanganate, to reduce the chromic acid. Finally, we titrate the excess of the ferrous salt added, by means of permanganate. The amount of chromium present is calculated from that of the ferrous salt oxidised by the chromic acid, which is itself given by the difference between the amount of permanganate corresponding to the volume of ferrous salt introduced and that absorbed by the solution.

The following equations explain these reactions:—

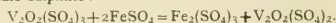
1. Estimation of the Vanadium:—



2. Estimation of the Chromium:—



In reality we do not titrate the ferrous sulphate in excess, but the divanadyl sulphate resulting from its action on the vanadic sulphate:—



The consideration of this equation and of Equation 1 shows that the final result is exactly the same, the divanadyl sulphate reducing the same amount of permanganate as the ferrous sulphate which brings it into existence.

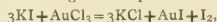
The results of this method are not influenced by the presence of small quantities of iron in the state of ferric sulphate in the original solution. When the proportion of chromium is much greater than that of the vanadium, it is necessary to use only a small quantity of the material, as the green colour of the sulphate of chromium tends to diminish the sensitiveness of the appearance of the rose tint due to a slight excess of permanganate.

The results obtained by observing this precaution are as exact as those which could be obtained by applying each of the two processes used separately, and which are very exact even by themselves.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 16.

THE IODOMETRIC DETERMINATION OF GOLD IN DILUTE SOLUTION.*

By RALPH N. MAXSON.

In a former paper from this laboratory (Gooch and Morley, *Am. Journ. Sci.*, 1899, viii., 261) it was shown that, under suitable conditions, potassium iodide acts normally upon auric chloride according to the equation—



and it appeared that this reaction may serve as the basis of a trustworthy method for the determination of small quantities of gold—the freed iodine being estimated by careful bleaching with sodium thiosulphate and the final addition of standard iodine to the incipient coloration of the starch indicator, rose in most cases, or only blue at the outset when the starch has not undergone hydrolytic change (Hale, *Am. Journ. Sci.*, 1902, xiii., 379). Three series of experiments were made upon solutions of auric chloride standardised by the ferrous sulphate method and by the method of Vanino (*Ber.*, xxxi., 1763), and one series upon auric chloride made from pure gold foil.

In the first series the solutions of auric chloride (0.8710 gm. to the litre), sodium thiosulphate (nearly N/100), and iodine (nearly N/100) were of such strength that an inaccuracy of 0.01 c.m.³ in measurement would correspond to about 0.00009 gm. for the gold solution and to a little more than 0.00001 gm. in terms of gold for each of the other solutions. It is hardly to be supposed that individual readings can uniformly approximate the truth within 0.01 c.m.³, and as there are six readings to be made in every complete determination, the chances for inaccuracy amounting to several hundredths of a milligram of gold—dependent to a great extent as to direction and amount upon the personal equation of the operator—are considerable. Should all these reasonable errors chance to lie in

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, [4], xvi., No. 92.

TABLE I.

Series	Number of determinations	Gold taken.		Strength of solutions.			Error. Average. M. grm.	Extremes.	
		M. grms.	M. grms.	Iodine.	Thiosulphate.	Gold.		M. grm.	M. grm.
I.	11	8.71	to 4.35	N/100	N/100	0.0871	-0.05	+0.03	-0.1
II.	20	0.87	to 0.087	N/100	N 100	0.00871	+0.02	+0.06	-0.02
III.	10	0.871	to 0.087	N 1000	N 1000	0.00871	+0.0001	+0.020	-0.020
IV.	14	0.520	to 0.052	N/1000	N 10000	0.052	+0.002	+0.01	-0.008

the same direction, the cumulative errors are likely to reach at least ± 0.00005 grm., and may be even more.

The actual error, due to all causes, found in the first series of twelve determinations, excepting a single determination manifestly not in line with the others, and tending to make the average error smaller, amounted in the mean to -0.00005 grm. of gold between extremes of $+0.00003$ and -0.00010 grm.

In the second series of twenty experiments, in which the solution of gold was ten times as dilute as in the experiments of the first series, the other solutions being of the original strength, the total average error actually observed was considerably lower, as would be expected, and amounted to $+0.00002$ grm. of gold between extremes of $+0.00006$ grm. and -0.00002 grm.

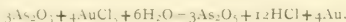
In a third series of ten experiments, in which the dilute gold solution (0.0871 to 1 litre) was used, nearly N/1000 iodine and nearly N/1000 thiosulphate were employed. The average error amounted to less than 0.000004 grm. between extremes of $+0.000020$ grm. and -0.000029 grm., but in these determinations the sensitiveness of the starch indicator to iodine becomes an important factor, and it was necessary to introduce a correction of 0.1 c.m.* for the amount of the N 1000 iodine necessary to bring out the starch reaction in the volume of liquid used when tested in blank.

In still another series of fourteen experiments, made upon a gold solution (0.0104 to 200 c.m.*), prepared by dissolving pure gold-foil in chlorine water and destroying the free chlorine by ammonia, the average error amounted to $+0.000002$ grm. between extremes of $+0.00001$ grm. and -0.000008 grm.

The results of these experiments may be summarised as shown in Table I.

It is plain that the average experimental errors, due to all causes, do not very much exceed the errors which might naturally be expected to arise from errors of reading. In repeating the work of Gooch and Morley I have obtained results of a reasonably similar order of accuracy. The process has, however, been recently criticised unfavourably by Rupp (*Ber.*, xxxv., 2011) on the ground that the percentage errors are found to be large. It is to be noted, however, that large percentage errors are inevitable in the application of volumetric methods to the determination of total weights measured in hundredths of a milligram, or tenths of a milligram, or even in a few milligrams, inasmuch as the reasonable errors to be expected in the measuring of solutions strong enough to be visibly reactive are of themselves large when reckoned as percentages of small absolute amounts. These errors, small as they are, Rupp attributes to the secondary reactions of potassium iodide on aurous iodide, in which gold is reduced and iodine set free. I have been unable, however, to find evidence of such action under the conditions of experimentation during periods much longer than those required for the completion of the analytical process. Thus aurous iodide, obtained by treating a solution of auric chloride containing 0.025 grm. of gold, with potassium iodide according to the directions of Gooch and Morley, adding starch, and bleaching the starch with sodium thiosulphate, gave no colour of starch blue after the interval of an hour. A second similar experiment gave the same result. Inasmuch as an interval of ten minutes is enough for the complete manipulation of a single determination, it is plain that the stability of the aurous iodide does not figure in the accuracy of the determination of the small amounts of gold for which the process was designed.

As a substitute for the method described by Gooch and Morley, and sustained by the fifty-five analytical determinations mentioned, Rupp announces a process for the estimation of gold depending upon the precipitation of that element from auric chloride by means of standard arsenious acid in excess, according to the equation—



and the titration of the excess of arsenious acid by iodine. To show the reliability of the process Rupp cites six determinations, in one of which the titrations were made in two portions. Four of these six deal with 6.12 m.grms. of gold each, while in two the gold amounted to 6.1 m.grms. These figures, which cover the entire range of the amounts used in Rupp's analytical determinations, do not represent the order of magnitude or range of the amounts of gold handled by Gooch and Morley, which varied from 8.7 m.grms. to 0.052 m.grm. Only two determinations upon amounts comparable with those used by Gooch and Morley were made, and in only these two were suitably dilute solutions of iodine (N/100) and of arsenious acid (N/100) employed.

The gold solution employed in all the determinations was of such strength that a single error of 0.01 c.m.* in reading would amount to an error of 0.00006 grm. of gold; while the arsenious acid employed in three determinations was so strong (N. 2) that an inaccuracy in reading to the extent of 0.01 c.m.* would introduce an error of 0.0003 grm., actually greater than the whole amount of gold involved in each of the individual determinations of the greater part of the entire series of Gooch and Morley, and nearly six times greater than their minimum amounts. It is plain, therefore, that Rupp's experiments do not relate to the small amounts of gold handled by Gooch and Morley, and that experiments made with such solutions as Rupp employed cannot form a basis upon which to found a method for the determination of the very small amounts of gold determined by Gooch and Morley.

It has seemed to be desirable, therefore, to submit the process of Rupp to further investigation. In these experiments the procedure of Rupp was followed in general, but the reagents were all used in solutions reasonably dilute, as must be the case if accuracy is to be attained. The gold solution used was prepared from pure gold chloride, and was carefully standardised by means of metallic magnesium, and electrolytically with the revolving cathode, according to the method of Gooch and Medway (*Am. Journ. Sci.*, 1903, xv., 320). The solution contained 0.0580 grm. of metal in 1 litre, and was free from nitric acid. The arsenic solution was N/100, and was made by properly diluting a standard solution of N/10 arsenious oxide. The iodine solution used was approximately N/100, and was made by properly diluting an iodine solution, which had been carefully standardised against the N/10 arsenic solution mentioned above.

In reducing and determining the gold the procedure was as follows:—A measured quantity of the slightly acid solution of standard auric chloride was drawn from a burette into a 100 c.m.* graduated flask, and to this was added a measured excess of a standard solution of arsenious acid dissolved, as usual, in acid potassium carbonate. In every case the excess of the arsenious acid was considerable, and the acid carbonate introduced simultaneously was enough to more than neutralise the slight acidity of the auric chloride. Rupp states that the reduction takes place in acid solution, but I have been unable to effect the precipitation of the gold when free acid is present, but from a

solution made so acid that the carbonate present in the standard arsenic is insufficient to neutralise the free acid, the gold may be precipitated upon the further addition of a suitable amount of acid potassium carbonate. The flask containing the gold, the arsenite, and the acid carbonate was heated thirty minutes upon a steam-bath, then cooled and filled to the 100 c.m.³ mark. Measured portions of the solution, 25 c.m.³ each, were titrated with the standard iodine in presence of acid potassium carbonate and potassium iodide. The details of these experiments are shown in Table II.

TABLE II.

Experi- ment.	Fraction titrated.	Gold found in each fraction. Grm.	Gold computed for the whole solution. Grm.	Gold taken. Grm.	Error. Grm.
I. One-fourth		0.00010	—	—	—
"		0.00011	—	—	—
"		0.00013	—	—	—
—		—	0.00045	0.00087	-0.00042
II. One-fourth		0.00010	—	—	—
"		0.00013	—	—	—
"		0.00010	—	—	—
—		—	0.00044	0.00087	-0.00043
III. One-fourth		0.00017	—	—	—
"		0.00016	—	—	—
"		0.00014	—	—	—
—		—	0.00063	0.00087	-0.00024
IV. One-fourth		0.00060	—	—	—
"		0.00060	—	—	—
"		0.00062	—	—	—
—		—	0.00242	0.00232	+0.00010
V. One-fourth		0.00056	—	—	—
"		0.00058	—	—	—
"		0.00058	—	—	—
—		—	0.00229	0.00232	-0.00003
VI. One-fourth		0.00043	—	—	—
"		0.00043	—	—	—
—		—	0.00172	0.00232	-0.00060
VII. One-fourth		0.00075	—	—	—
"		0.00074	—	—	—
"		0.00074	—	—	—
—		—	0.00297	0.00232	+0.00065
VIII. One-fourth		0.00061	—	—	—
"		0.00058	—	—	—
—		—	0.00238	0.00290	-0.00052
IX. One-fourth		0.00082	—	—	—
"		0.00081	—	—	—
"		0.00080	—	—	—
—		—	0.00324	0.00290	+0.00034
X. One-fourth		0.00072	—	—	—
"		0.00073	—	—	—
—		—	0.00290	0.00290	0.00000
XI. One-fourth		0.00066	—	—	—
"		0.00071	—	—	—
"		0.00075	—	—	—
—		—	0.00283	0.00290	-0.00007

A comparison of the figures obtained in the individual titrations of portions of a single reduction show that the difference due to the errors of analysis are reasonably small, rarely exceeding a few units in the fifth decimal place—or a few hundredths of a milligram. The errors of the process, however, computed by comparing the average of these single determinations with amount of gold actually taken, range from -0.6 m.grm. to +0.65 m.grm., are wholly irregular, and are approximately ten times as large, reckoned absolutely or in percentages, as the errors obtained by Gooch and Morley when handling similar amounts of gold. So far as the evidence of these experiments goes, it is plain

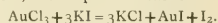
that the process of Rupp is wholly untrustworthy for the determination of the very small amounts of gold concerned.

I take this opportunity to thank Prof. F. A. Gooch for much kindly aid and advice in the preparation of this paper.

THE LIMIT OF ERROR IN THE VOLUMETRIC DETERMINATION OF SMALL AMOUNTS OF GOLD.*

By RALPH N. MAXSON.

In a former paper from this laboratory, Gooch and Morley (*Am. Journ. Sci.*, 1899, [4], viii., 261) established the accuracy of a method for the determination of small amounts of gold, based upon the reaction—



Recently the attempt has been made by Rupp (*Ber.*, xxxv., 2011) to show that this method is inaccurate, and to bring forward a process based upon the reduction of gold by standard arsenious acid, and titration of the residual arsenious acid by standard iodine. In a study of these two methods (*Am. Journ. Sci.*, 1903, [4], xvi., 155), I have verified the results obtained by Gooch and Morley, but have been unable to determine similar amounts of gold with even approximate exactness by the method of Rupp.

More recently, Rupp (*Ber.*, xxxvii., 3961) has disclaimed accuracy for his method when applied to amounts less than a few milligrams, and proceeds to discuss the absurdity of attempting to determine volumetrically tenths and hundredths of a milligram of material, however accurate the method may be—and this in the face of his statement, in his own previous paper, of volumetric results carried to thousandths of a milligram.

While quite in agreement with Rupp so far as to admit the absurdity of attempting to determine amounts of material measured in tenths and hundredths of a milligram by means of N/2 arsenious acid, as did Rupp in three out of the six determinations upon which he rested his process, I take the view, that with properly made standard solutions of suitable dilution, it is quite possible for a skilful analyst to determine tenths and hundredths of a milligram of material.

By the use of approximately N/100 iodine and thiosulphate, Gooch and Morley got results with a mean error of 5/100 milligram. between extremes of +3/100 milligram. and -10/100 milligram. in twelve determinations, a single small divided drop of the iodine solution and of the thiosulphate solution being sufficient to produce an immediate reaction with starch, and a bleaching of the starch colour, respectively.

When using N/1000 solutions of iodine it was necessary to add to the volume used 0.1 c.m.³ of iodine, in order that the first small drop of gold should bring out the starch reaction. This was a perfectly definite correction, and was equivalent to 1/100 milligram. of gold. With N/1000 solutions and with the application of this correction, ten experiments gave a mean error of less than 4/1000 milligram. between extremes of +2/100 milligram. and -29/1000 milligram; while in another series of experiments in which the start was made with pure gold foil, dissolved in chlorine water and treated by a process carefully described, the average error of fourteen determinations was +2/1000 milligram. between extremes of +1/100 milligram. and -8/1000 milligram. This is not theory; it is experiment. Here are volumetric solutions capable of showing 1/100 milligram., or less, of gold. Is it any more absurd to determine gold in this manner than to weigh that element upon an assay balance sensitive to 1/100 of a milligram? To be consistent, Rupp should include all processes, gravimetric as well as volumetric, in his sweeping declaration.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, xvii., No. 102.

The fact that large percentage errors occur in certain determinations made by Gooch and Morley, upon small amounts of gold, is again made the subject of criticism by Rupp.

As I have previously stated, every analytical process has a certain inevitable error, and because of this fact as we approach the limit of accuracy of the process the percentage error will increase rapidly. This increase can, however, under no circumstances be considered a reason why small quantities of substances should be disregarded in analysis, either volumetric or gravimetric. Because the ordinary analytical balance is sensitive only to 1/10 or 1/20 milligram, is no reason for declining to weigh tenths or twentieths of a milligram, although the percentage error in weighing such amounts may be very large.

Besides these wholly unreasonable criticisms, reference is made by Rupp to some matters of scientific fact, and to these I next propose to give attention.

To Rupp's statement that with dilute solutions the starch indicator is no longer reliable, it is sufficient to reply that experience has shown that one small drop of N/100 iodine solution develops the starch colour at once, in solutions of the volume and concentration described; and if N/1000 solutions be used, a perfectly definite, and not excessive allowance of 0.1 c.c., equivalent only to 1/100 milligram, of gold, is all that is needed.

Further, Rupp claims that the decomposition of aurous iodide is the greatest error of the process of Gooch and Morley, and refers to the handbooks of chemistry to substantiate this opinion. No handbooks are known to me which discuss the deportment of aurous iodide under exactly the conditions of this analytical process, but a study of the reaction, of which I made mention in a former paper (*loc. cit.*), showed that aurous iodide possesses stability sufficient for the purposes of the analytical process.

I have, however, thought the matter of sufficient interest to warrant further investigation concerning the deportment of this salt under more varied conditions.

The method employed to determine the rapidity with which the aurous iodide decomposes was as follows:—A measured quantity of a standard gold solution was drawn off into a beaker and diluted to the required volume. To this was added the necessary amount of a solution of pure and specially prepared potassium iodide, starch was added, and the freed iodine immediately treated with N/100 thio-sulphate solution, but only to the rose tint, so that, as in the actual analysis, there might be no decomposing action due to an excess of thio-sulphate upon the aurous salt.

The time was noted and the mixture allowed to stand until the iodine freed by the decomposition of the aurous iodide had brought the colour of the liquid to an ordinary starch blue. The data obtained in this manner are shown in the following table. The gold solution used contained 0.00048 grm. of metal to the cubic centimetre.

It may be seen from these results that the decomposition of the aurous iodide under the conditions is comparatively slow, although potassium iodide was present in large excess. In these experiments the colouration ran through various gradations from pink to blue, as the starch used, in common with most specimens, had suffered hydrolytic change, the pink colour indicating, of course, the incipient excess of iodine, and not under-titration as Rupp has stated (see Hale, *Am. Journ. Sci.*, 1902, [4], xiii., 390).

As I have previously shown, a complete determination by the method of Gooch and Morley can be easily accomplished in ten minutes; the maximum time actually necessary for the completion of the titration after the formation of the aurous iodide need not exceed four minutes. As can be seen from the experiments tabulated above, the minimum time required for the incipient decomposition of the aurous iodide was seventeen minutes. In no case did decomposition take place immediately, although potassium iodide was present in large excess. It is to be especially noted that these experiments begin where the analytical process ends, so that the probability of any iodine being freed by a too rapid decomposition is rendered yet more remote. The facts, then, afford absolutely no foundation

No.	Gold.		KI.	Volume before the addition of thio-sulphate		Time in minutes necessary to give blue colour.
	Grm.	C. m. s.		Grm.	C. m. s.	
1.	0.0144	0.20		50		19
2.	0.0144	0.20		50		47
3.	0.0144	0.20		50		95
4.	0.0144	0.20		50		150
5.	0.0144	0.20		50		115
6.	0.0144	0.20		50		82
7.	0.0144	0.20		50		50
8.	0.0096	0.08		50		17
9.	0.0096	0.08		50		95
10.	0.0096	0.08		50		28
11.	0.0096	0.08		50		78
12.	0.0096	0.08		50		18
13.	0.0096	0.08		50		30
14.	0.0096	0.08		50		36
15.	0.0096	0.08		50		32
16.	0.0048	0.05		50		45
17.	0.0048	0.05		50		168
18.	0.0048	0.05		50		25
19.	0.0048	0.05		50		48
20.	0.0048	0.05		50		43
21.	0.0024	0.05		50		95
22.	0.0024	0.05		50		105
23.	0.0024	0.05		50		135
24.	0.0024	0.05		50		None in 3 hours
25.	0.0024	0.05		50		None in 3 hours
26.	0.0014	0.01		35		130

for the statement that the decomposition of aurous iodide is an inherent source of error in the method of Gooch and Morley.

Concerning the accuracy of the method proposed by Rupp it is unnecessary to speak further, since Rupp now disputes the desirability of estimating less than the milligram; but to the reduction of gold chloride by arsenious oxide, the reaction used by Rupp, it is necessary to recur. Rupp states that the process of reduction goes on in acid solution. As I said in a former paper, I have been unable to effect the precipitation of the gold when free acid is present, but after the addition of acid potassium carbonate reduction takes place. Rupp added to his solution of gold chloride containing hydrochloric acid 10 c.m. of nearly N/2 solution of arsenious oxide. It is to be supposed that this solution of arsenious oxide was made, as usual, by dissolving the oxide in acid potassium carbonate. The question arises as to whether Rupp did not have enough acid carbonate in his arsenic solution to neutralise the free acid. The fact that the gold was precipitated, and within ten or fifteen minutes, points strongly, according to my experience, to an alkaline condition of the solution. So, if to heat a solution of acid potassium carbonate upon the water bath, under the experimental conditions, brings about the formation of an iodine-binding carbonate, and is indeed an error as Rupp says, it would seem that Rupp makes that error. But was it an error? It has seemed worth while to investigate this point.

A N/10 arsenic solution was prepared, as usual, with the aid of 20 grms. of potassium acid carbonate to the litre. Twenty-two c.c. of this solution were drawn off and titrated with an approximately N/10 iodine solution in the usual manner. Four lots of this arsenic solution of 22 c.m. each were then carefully drawn off and heated upon the steam bath for thirty minutes, and when cool were titrated against the above-mentioned iodine solution. The volume of the solutions used in these experiments was in all cases approximately 75 c.c. The results obtained are given in the accompanying table:—

Standard As ₂ O ₃ taken.	Iodine used to titrate at once.	Iodine used to titrate after heating one-half hour on the water bath.
C. m. s.	C. m. s.	C. m. s.
22.0	22.08	22.10
22.0	22.07	22.08
22.0	22.08	22.09
22.0	22.07	22.08

These figures show conclusively that acid potassium carbonate in solution of the concentration used in these experiments, 0.44 gm. in a volume of 75 c.c., does not in thirty minutes heating upon the water bath undergo such change as to cause it to absorb an appreciable amount of iodine in the following titration. Just what the effect may have been in Rupp's experiments cannot, of course, be determined in the absence of knowledge in regard to the acidity of his gold solution, and the alkalinity of his arsenic solution.

In conclusion it is obvious that the criticisms made by Rupp are not warranted by the facts. While, as its author now concedes, the method proposed by Rupp is not to be considered of value for the determination of small amounts of gold, all the evidence goes to show that the process of Gooch and Morley is accurate, and in the hands of a skillful analyst, adapted to the estimation of minute quantities of gold.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 28, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A PAPER ON "An Interference Apparatus for the Calibration of Extensometers," by Mr. JOHN MORROW and Mr. E. L. WATKIN, was read by Mr. MORROW.

The paper describes an apparatus for calibrating extensometers and similar instruments by comparison with the wave-length of sodium light. The apparatus is self-contained and easily made ready for use. It is capable of great accuracy, as it is unaffected by external disturbances, accidental displacements, or errors due to backlash in the apparatus itself. It consists essentially of two metal cylinders of equal diameter, with their axes in the same straight line, but with a small gap between their adjacent ends. The gap is increased or decreased by the movement of a lever actuating a screw, and the alteration in its amount is measured by the interference rings produced in an optical system situated inside the gap.

The extensometer is attached by its gauge-screws to the metal cylinders, and provides a second method of determining their relative axial displacement. The two sets of readings are taken simultaneously, and are compared. The points examined in any strain-meter are (a) the magnification constant, (b) the action at starting and reversing, and (c) the proportionality of reading to displacement. The experiments were made on an extensometer of the differential mirror type described by one of the authors.

Prof. S. P. THOMPSON said he was pleased to see that optical devices were being applied practically for measuring small lengths and for testing extensometers. It was a step in the direction of realising Maxwell's idea regarding the utilisation of the wave-length of light as a standard of length. He would like to know the "order" of the rings which were used in the experiments, and also if there was any difficulty due to the interference of the light emitted by the two sodium lines. It would be interesting to know how the authors had measured fractions of a ring, and what fraction of a ring it was possible to measure with accuracy.

The CHAIRMAN said the method employed was similar to that used by Fizeau; a method carried to perfection by Benoit in the measurement of the coefficient of expansion of small objects. The principle had been applied by the authors to practical mechanical problems.

Mr. MORROW, in reply to Prof. Thompson, said the rings used were near to the centre of the system. In fact, the two surfaces could be brought into contact and the experiments commenced from that position. Fractions of a ring

were estimated by eye, but there would be no difficulty in employing an eyepiece with a micrometer-scale. It was easy to estimate to one-tenth of a ring with the apparatus shown, but no mechanical device was accurate to anything like the same extent.

A paper on "A Sensitive Hygrometer," by Dr. W. M. THORNTON, was read by the Secretary.

The instrument is made by enclosing the cooled surface of a Regnault's hygrometer in a glass globe so that only the mass of vapour contained in the vessel is available for condensation. The cooled surface is made much smaller than usual—about 1 sq. c.m. The surface-density of the deposited moisture depends on the total quantity of water-vapour present. If this is more than a minimum to be determined later, it will be visible either by the loss of brightness by scattering, or by observing, as in the Dines hygrometer, the scattered light itself. Little is known as to the manner in which moisture is deposited on smooth cold surfaces. Dr. Park has shown that the thickness of the deposit is of the same order as that of the black spot in interference-films. The reflection of light from such a clear layer of uniform thickness backed by a bright surface is considered in the paper, and it is shown that the loss of light due to the thinnest possible films can be perceived. The opposite case to that of a smooth layer is that of clear spherical particles resting on the surface. This is also considered, and the surface-density to give a visible deposit is calculated. In connection with an interesting note was received from Lord Rayleigh in reply to an inquiry, in which he shows that the maximum brightness of a cloud is about 4×10^{-4} that of the sun. Comparing all values it is taken that 10^{-8} grms. per sq. c.m. can be detected by unaided vision with diffused light. The time taken for moisture to diffuse from a state of uniform distribution throughout the globe towards the centre is then calculated, and found to be less than ten minutes for a sphere of 20 c.m. diameter. In the experimental instrument an ether spray was directed on to the inner surface of a silver cap at the end of a steel tube. The latter is surrounded by a glass tube and air space, so that only the cap is exposed to the gas in the globe. Air dried in the usual way by passing slowly through tubes of sulphuric acid and phosphorus pentoxide was moist enough to dim the cap. For very dry gases it is suggested that liquid air might be used as a cooling agent. The paper is an attempt to make the somewhat neglected Regnault hygrometer an instrument of precision in the detection of small quantities of moisture. There is no other method known to the author by which this can be done, except in certain cases by the occurrence of chemical reaction causing a change of colour.

Dr. CHREE remarked that unless there were some means of recording the temperature of the metal on which the moisture was deposited, he did not see how absolute results could be obtained, and that unless numerical results were obtainable the sphere of usefulness of the instrument was likely to be limited. The ordinary methods of obtaining hygrometric results, viz., by wet and dry bulb hygrometers or by the hair hygrometer, left a good deal to be desired, especially at temperatures below $0^{\circ}\text{C}.$, so that there was an opening for an accurate hygrometer if not too complicated.

Prof. F. T. TROUTON said he had lately been making experiments bearing on the subject of the paper. He was engaged in determining the electrical resistance between electrodes fixed upon the surface of glass. At present he was investigating the resistance with the temperature of the glass well above the dew-point, and he found that it varied in a complicated manner with the time the current was allowed to pass. When the air was near the dew-point the variation of the resistance was altogether different in character from the variation when the air was far from saturation. The sudden variation in resistance when moisture was deposited upon the surface of the glass gave an accurate method of determining the dew-point.

The SECRETARY said the author had tried to make the instrument quantitative by determining the minimum

quantity of moisture which could be detected, and also by observing the time which elapsed before all the moisture was deposited.

A "Note on a Property of Lenses," by Dr. G. E. ALLAN, was read by the Secretary.

A well-known method of testing the concavity or convexity of a lens consists in holding the lens at arm's length, and, while looking through it, moving it from side to side or up and down, when the image in the convex lens is found to move in the opposite direction to that of the lens, whilst in the case of the concave lens it moves in the same direction. The above facts hold if, instead of the naked eye, we employ a microscope. If the division marks of a scale be looked at through a lens of considerable focal length, and the lens be at the same time moved across the field of view, it is seen that the motion of the lens is much greater than that of the image, and the disparity of the two motions is greater the nearer the lens is to the scale and the flatter the lens. It is shown that the focal length of a lens can be expressed as the product of the distance from the scale to the lens and the magnification, the magnification being defined as the ratio between the displacement of the lens and the displacement of the image. The results obtained by applying the method to the determination of the focal lengths of three lenses are given in the paper.

Mr. T. H. BLAKESLEY said he was aware of the method described by the author, which, with limitations, was accurate enough for the determination of focal lengths above 50 or 60 c.m. He pointed out that the formula given in the paper was not, in general, quite rigorous. The distance required was not from the scale to the lens, but from the scale to the first principal point. This difficulty could be easily overcome by making two experiments with different distances between the scale and the lens.

NOTICES OF BOOKS

Small Destructors for Institutional and Trade Waste. By W. FRANCIS GOODRICH, Assoc. Inst. Mech. Engineers, &c. With twenty-eight illustrations. London: Archibald Constable and Co., Ltd. 1904.

DESTRUCTORS for waste products of all kinds are coming more and more into vogue, and while those for civic use are multiplying rapidly there is also a growing demand for the smaller prototype—the destructor for dealing with institutional and trade refuse. These small destructors have not been discussed in the various books which have already appeared on refuse disposal; hence the present work.

This volume is intended for the use of architects, medical superintendents, and large manufacturers, and all who are concerned in the sanitary disposal of the waste produced in hospitals, infirmaries, asylums, convalescent homes, hotels, &c., where the available waste may be turned to profitable account for power production.

The book consists of six chapters, the first being introductory. In Chapter III. institutional destructors are described and illustrated, and Chapter IV. deals with portable destructors. Chapter V. is devoted to the American practice and the special features of the American designs, while in Chapter VI. the author discusses the disposal of trade refuse and its application to the production of steam power. The book is well printed and illustrated, and will no doubt be of considerable service to those in whose interests it is written.

We regret to point out that there is no index, though this loss is in part made up for by the table of contents.

The Electric Furnace. By HENRI MOISSAN. Authorised Translation by VICTOR LENHER, Ph.D., University of Wisconsin. Easton, Pa.: The Chemical Publishing Company. 1904.

The original French edition of this valuable work has been

already reviewed at length in the *CHEMICAL NEWS*, and we have but little to add to our previous remarks.

Since the publication of the French edition there has been a great development of certain industries in connection with the electric furnace, such as the preparation of calcium carbide, chromium, ferro-silicon, ferro-chromium, and ferro-titanium; while Mr. F. N. Acheson, in following up his discovery of the crystalline silicide of carbon, has been able to realise the industrial preparation of graphite.

The translator expresses his deep obligation to M. Moissan for the additional matter in manuscript, which is included in this translation, thereby bringing the work up to date.

The book is divided into four chapters. In the first the different forms of electric furnaces are described. Chapter II. contains the study of three forms of carbon—amorphous carbon, graphite, and diamond.

The third chapter gives the preparation of a number of elements by means of the electric furnace, and the fourth contains researches on a number of new binary compounds, the carbides, silicides, borides, phosphides, arsenides, and sulphides; while general conclusions complete the work.

It is a common fault in French books to be without an index; we are sorry the translator has not seen his way to prepare one for this English edition, which suffers from the omission. Apart from this we have no fault to find with the book.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade, unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxiv., No. 15, October 10, 1904.

The Transition Temperatures of Steels.—Georges Charpy and Louis Grenet.—The transition temperatures of certain carbon steels have lately been determined by studying the variation with temperature of their electric resistance, thermo-electric power, and rate of expansion or contraction. Transition temperatures obtained by the electric resistance method and by dilatometry agree within the limits of experimental error.

Percentage of carbon.	Transition temperature.			
	Electric resistance method.		By contraction.	
	Beginning	End.	Beginning	End.
0.82	730	760	735	745
1.06	730	760	740	750
1.15	739	739	735	740
1.38	750	750	735	755

Results obtained by thermo-electric and dilatation methods do not show much agreement, except in the case of the softest steels.

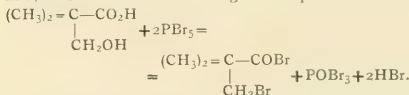
Substitution Derivatives of Phenyl diazoaminebenzene.—Leo Vignon and M. Simonet.—When certain substituted anilines react upon diphenylamine, substituted derivatives of phenyl diazoaminebenzene are obtained. The method of preparation is as follows:—The amines are diazotised as hydrochlorides, then treated with diphenylamine in alcoholic solution in the presence of carbonate of soda. The temperature is kept between 4° and 5°. The diazoamine formed is precipitated with water and excess of ice, and extracted with ether. The ether is dried over solid K_2CO_3 and evaporated, leaving behind the phenyl diazoaminebenzene derivative. In this way *o*-, *m*-, and *p*-nitro-, $[NO_2C_6H_4 \cdot N \cdot N \cdot C_6H_5]_2$, *o*-, *m*-, and *p*-chloro- and bromo-, *p*-iodo-, and methoxyphenyl diazoaminebenzene have been prepared; di- and trichloro- and bromo-derivatives have also been obtained. All these substances have the general properties of diazo-derivatives.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxxi., No. 4.

Action of Carbonic Acid on Aqueous Solutions of Aniline in the presence of Nitrites.—Louis Meunier.—Already noticed.

Bromopivalic Acid and its Derivatives.—E. E. Blaise and L. Marcilly.—The authors have succeeded in preparing bromopivalic acid indirectly by treating oxypivalic acid with pentabromide of phosphorus. To 2 molecules of pentabromide of phosphorus they added, a little at a time, 1 molecule of oxypivalic acid; hydrobromic acid is given off, and the mass gradually becomes liquefied. It was heated on the water-bath to complete the reaction and to drive off a portion of the hydrobromic acid, which was formed according to the equation—



The liquefied mass was poured into water and partially neutralised with carbonate of sodium, still leaving some free hydrobromic acid. Exhaust three times with a large volume of ether; this solution is then dried, filtered, and evaporated. The residue consists of an oil which crystallises in a few days when kept protected from moisture. This product was distilled at 143–145° under 33 m.m., and it crystallised on cooling. It is very soluble in alcohol, ether, and most of the solvents. By etherification this bromopivalic acid gives bromopivalate of ethyl, identical with that obtained direct from the action of pentabromide of phosphorus on oxypivalate of ethyl. Several other derivatives are described, such as phospho di-oxypivalic acid, phospho di-oxypivalate of potassium, &c.

The β-Aldehyde Ethers.—E. E. Blaise and L. Marcilly.—The condensation of formate of ethyl with the ethers of the fatty acids cannot be effected except when the α-carbon atom has 2 atoms of hydrogen; thus the method cannot lead to the formation of β-aldehyde acid with a true aldehydic function. On the other hand, the authors have attempted to obtain these compounds by the careful oxidation of the α-dialcylhydracrylic acids, and their examination is a matter of great interest particularly as regards the possible parallelism of their properties with those of the β-ketonic ethers. The result of their research is to show the very great analogy between the β-aldehydic ethers and the β-ketonic ethers.

Acetones with an Acetylenic Function. New Method for the Synthesis of Pyrazols.—Charles Moreau and Maurice Brachin.—Already noticed.

Bismuthoprotocatechuic Acid.—Paul Thibault.—The author has prepared a well-crystallised bismuthoprotocatechuic acid having the formula $\text{C}_7\text{H}_5\text{O}_5\text{Bi}$, by the direct treatment of protocatechuic acid with pure hydrated oxide of bismuth; he has also obtained a few other derivatives of this acid, its sodium, potassium, and ammonium salts and its anilide. The preparation of these compounds has enabled him to determine the formula which should be given to this compound.

An Isomer of Borneol, Camphenolic Alcohol, and some Camphenolic Derivatives.—A. Béhal.—Camphenolic alcohol was prepared by mixing camphenolate of ethyl in a flask with half its weight of absolute alcohol; a vertical condenser is fitted and the sodium added all at once. The reaction is very lively. If a little sodium remains, add absolute alcohol until it has all disappeared. At this moment add, gradually, 50 grms. of water and heat to boiling for a quarter of an hour. Distil off the bulk of the alcohol on a salt bath, then continue the distillation with a current of steam so long as any oil remains on the surface. Exhaust the distillate with ether and dry over sulphate of sodium. Distil the ether, and rectify the residue at the ordinary pressure. The product is obtained

pure the first time. The cooled alkaline residue, treated with ice and acidulated with dilute hydrochloric acid, gives inactive camphenolic acid in a pure state. The author then describes the preparation and properties of several camphenolic derivatives.

Action of Laccase on Gaiacol.—Gabriel Bertrand.—Already noticed.

Stimulating or Paralysing Influences acting on Manganese regarded as an Oxygen Carrier.—A. Trillat.—Already noticed.

Production and Distribution of some Organic Substances in the Mandarin Orange Tree.—Eug. Charabot and G. Laloue.—From a number of experiments tried and fully described in this paper the authors have drawn the following conclusions:—The volatile acidity in the mandarin orange tree gets less from the leaf to the wood. In the same organ it is greater when this latter is young than when its development is more advanced. But in absolute value the amount of volatile acid is greater in an old leaf than in a young one, which shows that it is formed at a greater rate than it disappears.

MISCELLANEOUS.

Historical Medical Exhibition—Postponement.—Mr. Wellcome writes to say that the response to the announcement of the proposed Historical Medical Exhibition has been beyond his expectations, and this, together with the many valuable suggestions received from leading members of the profession and the trade, at home and abroad, has prompted him to considerably widen its scope. The extent of the work involved renders it impossible to fix a definite date for the exhibition until a later period, announcement of which will be duly made. Although in one sense, he regrets this delay, it will, on the other hand, enable him to make the exhibit more comprehensive and complete, and to include many objects of exceptional interest that have been promised from different quarters of the globe.

Society of Arts.—The Society of Arts will commence its fourth half-century on the 16th, when Sir William Abney, as Chairman of the Society's Council, will open the 151st Session with an address. The subjects on which papers will be read at the meetings before Christmas include British Trade, Canals, the St. Louis Exhibition, Patent Law, Burma, and Street Architecture. There will also be a course of lectures on wind instruments, with musical illustrations.

Royal Institution.—A Christmas Course of Lectures (adapted to a Juvenile Auditory) will be delivered by Mr. Henry Cunynghame, C.B., on "Ancient and Modern Methods of Measuring Time" (Experimentally Illustrated). The dates of the Lectures are December 27, 29, and 31, 1904; January 3, 5, and 7, 1905.

Examination of Liquid Crystals by means of Electrical Cataphoresis.—G. v. Bredig and G. v. Schukowsky.—If the liquids to which Lehmann has given the name liquid crystals are actually suspension or emulsion mixtures, as Tammann and G. Quincke suppose, they would, like these suspensions in nearly all cases, be cleared and separated by cataphoresis, i.e., the migration of the suspended particles in the electric current. The authors have applied this method of examination to five different turbid, double refracting liquids, obtaining their current either (1) from an accumulator battery of 72 volts or (2) from the secondary coil of a large inductor with mercury interrupter, and have found that generally no clearing of the liquid occurs. Thus the result of the electrical examination of liquid crystals does not confirm the view that they are emulsions or suspensions, but shows that probably they are definite chemical individuals possessing specific optical properties.—*Berichte*, xxxvii., No. 13.

Awards at the St. Louis Exhibition.—Messrs. Boake, Roberts, and Co. have received a Grand Prize, Two Gold Medals, and one Silver Medal, for their award at the St. Louis Exhibition. They exhibited Sulphurous Acid, Sulphites of Sodium, Potassium, Calcium, and other bases, in addition to their liquid SO₂ in syphons for college and lecture use. They also exhibited Phosphoric Acid, special Phosphates for pharmaceutical purposes, Hydrofluoric Acid, Metallic Fluorides, and Caramels and Colourings for all purposes.

The London Essence Company have forwarded us a copy of No. 4 of their half yearly reports. This number contains the results of their investigations on the high boiling constituent common to oils of lemon and limes; the research has resulted in the discovery of a new sesquiterpene, probably of the type of the olefinic sesquiterpene, and has also resulted in showing that terpineol is a constituent of lime oil. There are also a number of other interesting notes on essences, oils, &c., that will well repay reading through.

Messrs. F. E. Becker and Co. (W. and J. George, Ltd., successors) have just issued a new Illustrated and Descriptive Catalogue of Physical Apparatus, &c., manufactured by them. This is the largest and best English catalogue of its kind printed, and comprises some 630 pages and over 4000 illustrations; herein will be found all the newest up to date apparatus with all the latest improvements as manufactured at their works, while all obsolete apparatus has been omitted. The whole catalogue is arranged in a very clear manner under a number of principal headings, such as Magnetism, Heat, Sound, Light, Mechanics, Electricity, Pneumatics, Meteorology, X-ray Apparatus, &c., and a good index is provided; in fact, everything possible has been done to make this as perfect a guide as possible to users of apparatus in the subjects touched upon.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst. Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. H.H. The Raj Rana Bhawani Singh Bahadur of Jhalawar, Mr. J. Jennings, and Mr. E. J. Preston were elected Members. It was announced that the Institution had received a bequest of £100 under the will of the late Miss Harriet Jane Moore. The special thanks of the Members were returned to Dr. Ludwig Mond for his donation of £755 for the purpose of erecting a lift from the basement to the second floor of the Institution, and any surplus after the completion of the work to go to the Research Fund. During the recess the entrances and exits of the Lecture Room of the Royal Institution have been materially improved by the erection of two covered-in iron staircases and the widening of the doorways, and the ceiling has been considerably raised.

MEETINGS FOR THE WEEK.

WEDNESDAY, 16th.—Microscopical, 8. "Theories of Microscopic Vision" (a Vindication of the Abb's Theory), by A. E. Conrady.

Society of Arts, 8. (First Ordinary Meeting). Inaugural Address of the 151st Session, by Sir William Abney, K.C.B., D.C.L., D.Sc., F.R.S., Vice-President and Chairman of the Council.

Chemical, 5.30. "Isomerism of the Amidines of the Naphthalene Series," by R. Meldola and J. H. Lane. "Theory of the Production of Mercurous Nitrite and of its Conversion into various Mercury Nitrates," by P. C. Ray. "Amidechlorides," by G. D. Lander. "New Synthesis of Isocaproaldehyde and some Derivatives," by D. T. Jones and G. Tattersall. "Influence of Substitution in the Nucleus on the Rate of Oxidation of the Side chain—II. Oxidation of the Halogen Derivatives of Toluene," by J. B. Cohen and J. Miller. "The Halogen Derivatives of Naphthacenequinone," by S. S. Pickles and C. Weizmann. "Constitution of Pyrazolidone Derivatives," by B. Prentice.

A Selection from MACMILLAN & CO.'S BOOKS FOR STUDENTS OF CHEMISTRY.

SECOND EDITION NOW READY.

THE PRINCIPLES OF INORGANIC CHEMISTRY. By WILHELM OSTWALD.

Translated with the Author's sanction by ALEX. FINDLAY,
M.A., Ph.D., D.Sc.
With 126 Figures in the Text. 8vo. 18s. net.

THIRD EDITION Entirely re-written and Enlarged. CHEMICAL TECHNOLOGY AND ANALYSIS OF OILS, FATS, AND WAXES.

By Dr. J. LEWKOWITSCCH, M.A., F.I.C., &c.
With 88 Illustrations and numerous Tables. Medium 8vo. 61s. top.
36s. net
NATURE.—"The standard English book of reference on the subject."

SECOND EDITION. TABLES FOR QUALITATIVE CHEMICAL ANALYSIS.

Arranged for the Use of Students.
By A. LIVERSIDGE, M.A., LL.D., F.R.S., Hon. F.R.S.E.;
Associate of the Royal School of Mines, London; Professor of
Chemistry in the University of Sydney.

. These Tables make a new departure in Qualitative Analysis, viz., by applying Quantitative methods to Qualitative Analysis. Special attention is paid to the reactions of the Rare Elements and to many common carbon compounds not usually included in such works.

FRACTIONAL DISTILLATION. By
SYDNEY YOUNG, D.Sc., F.R.S., Professor of Chemistry in University College, Bristol, With 72 Illustrations. Crown 8vo, 8s. 6d.

AN INTRODUCTION to the STUDY of
CHEMISTRY. By Prof. W. H. PERKIN, JR., Ph.D., F.R.S.,
and BEVAN LEAN, D.Sc., B.A. (Lond.). Globe 8vo, 2s. 6d.

A PRIMER OF CHEMISTRY. By Sir
HENRY E. ROSCOE, F.R.S. Illustrated. With Questions.
Fount 8vo, 1s.

INORGANIC CHEMISTRY FOR BEGIN-
NERS. By Sir HENRY E. ROSCOE, F.R.S. Assisted by
JOSEPH LUNT, B.Sc. Globe 8vo, 2s. 6d.

LESSONS IN ELEMENTARY CHEMIS-
TRY, INORGANIC AND ORGANIC. By Sir H. E. ROSCOE,
F.R.S. Sixth Edition, thoroughly revised. Fcap. 8vo, 4s. 6d.

INORGANIC CHEMISTRY FOR AD-
VANCED STUDENTS. By Sir H. E. ROSCOE, F.R.S., and
Dr. A. HARDEN. Globe 8vo, 4s. 6d.

A TREATISE ON CHEMISTRY. By Sir
H. E. ROSCOE, F.R.S., and the late C. SCHORLEMMER,
F.R.S. Completely revised by Sir H. E. ROSCOE, assisted by
Drs. H. G. COLMAN and A. HARDEN. 8vo. Vol. I. The Non-
Metallic Elements. 21s. Vol. II. The Metals. 31s. 6d.
Vol. III. The Chemistry of the Hydrocarbons and their Deriva-
tives, or Organic Chemistry. Parts II., IV., and VI., 21s. each.
Part III., 15s.

LESSONS IN ORGANIC CHEMISTRY.
By G. S. TURPIN, D.Sc. 2s. 6d.

A TEXT-BOOK OF INORGANIC CHE-
MISTRY. By Prof. IRA REMSEN. 8vo, 15s.

INORGANIC CHEMISTRY. By Prof. I.
REMSEN. Crown 8vo, 6s. 6d.

ORGANIC CHEMISTRY. By Prof. I.
REMSEN. Crown 8vo, 6s. 6d.

The ELEMENTS OF CHEMISTRY. By
Prof. I. REMSEN. 11th Impression. Fcap. 8vo, 2s. 6d.

COLLEGE TEXT-BOOK OF CHEMIS-
TRY. By Prof. I. REMSEN. Extra Crown 8vo, 8s. 6d. net.

MACMILLAN & CO., Ltd., LONDON.

IMPORTANT NEW SCIENCE BOOKS.

MATERIALIEN DER STEREOCHEMIE. Ed. C. A. BISCHOFF. 2 stout vols., 8vo, covering the period from 1894 to 1902. £4 10s.
PAULI (Dr. R.)—DIE SYNTHESE DER AZOFARBSTOFFE auf Grund eines symbolischen Systems. Large 8vo. £1 10s.
WOLFRUM (Dr. A.) CHEMISCHES PRAKTIKUM. 2 vols., 8vo, and an ATLAS in folio containing 721 ill. and 11 plates. Cloth. £1 18s.
TRAITE de CHIMIE MINERALE. Published under the Direction of HENRI MOISSAN, with the collaboration of the greatest Scientific Men. Vols. I and III. To be completed in 5 vols. Subscription Price for the whole work, £5 5s., which will be raised Dec. 1, 1904. Any other **BOOKS and PERIODICALS** (English and Foreign) reviewed in this Paper promptly supplied.

A. OWEN & CO.,English and Foreign Science Booksellers and Publishers.
286, HIGH HOLBORN, LONDON, W.C.**MELTING & BOILING-POINT TABLES.**

BY

THOMAS CARNELLEY,

D.Sc. (Lond.), B.Sc. (Vict.), F.C.S.,

Professor of Chemistry in University College, Dundee.

The Standard and only work upon the subject.

2 Vols. Ry. 4to. 799 pp. 42s.

HARRISON & SONS, Pall Mall, London, S.W.**E. GEORGE & SONS,**
BOOKSELLERS,

151, WHITECHAPEL ROAD, LONDON, E.,

Are OPEN to PURCHASE Complete Sets or short runs of the following:—*Chemical News, The Analyst Journal of the Chemical Society, 1848 to 1870, Journal of the Society of Chemical Industry, or the Publications of any other English or Foreign Learned and Scientific Societies.*—Libraries Purchased.

Current Catalogue of General Literature sent on application.

BRYAN CORCORAN Ltd

MILLSTONE BUILDERS,
WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.



Sole Makers of **MILBURN**
Patent Conoidal Stone Grinding Mills,
Especially suitable for certain materials, Wet or Dry.
Works and Warehouses: Back Church Lane.
Parcel Dept.: Basement of the Corn Exchange.
31, MARK LANE, LONDON.

MICA.Telephone
No. 2248
Avenue.**F. WIGGINS & SONS,** 10, Tower Hill, E., & London.**MICA MERCHANTS.**Manufacturers of Mica Goods or Electrical and ALL purposes.
Contractors to His Majesty's Government.**COVERS FOR BINDING.**Cloth, Gilt-lettered Covers for Binding the Half-yearly
Volumes of the**CHEMICAL NEWS**

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered
at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

ALDERSHOT GAS and WATER COMPANY.**SURPLUS TAR.**

The Directors are prepared to receive and consider Tenders for the Purchase of **SURPLUS TAR** (approximately 1200 Tons) produced at their Gas Works, Ash Road, Aldershot (private siding into works, Tongham Station, L.S.W.Ry.), for a year, from January 1st to December 31st, 1905. Specifications and conditions can be obtained on application to the undersigned.

Tenders to be sent in to the undersigned, endorsed "Surplus Tar," to arrive not later than 9 o'clock on the morning of **FRIDAY, December 2nd, 1904.**

The highest or any tender not necessarily accepted.

(By Order)

R. W. EDWARDS, Secretary.

November 8, 1904.

INSTITUTE OF CHEMISTRY
OF GREAT BRITAIN AND IRELAND.

Incorporated by Royal Charter.

NOTICE IS HEREBY GIVEN that the next **INTERMEDIATE EXAMINATION** will be held at the Laboratories of the Institute, commencing on **TUESDAY, the 3rd of JANUARY, 1905.**

Examinations in the following branches of the **FINAL EXAMINATION** for the **ASSOCIATESHIP (A.I.C.)** will be held in the Laboratories of the Institute, commencing on either **TUESDAY, the 3rd, or TUESDAY, the 10th of JANUARY, 1905:**—(a) Mineral Chemistry; (b) Metallurgical Chemistry; (c) Physical Chemistry; (d) Organic Chemistry. A Final Examination in Branch (e) The Analysis of Food and Drugs and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, will be held in the Laboratories of the Institute, commencing on **MONDAY, the 9th day of JANUARY, 1905.**

The Examinations are open only to Candidates who have complied with the Regulations.

Applications for registration to the above Examinations should be forwarded to the Registrar not later than **THURSDAY, the 1st of DECEMBER, 1904**, on which day the List of Candidates will be closed.

(By Order of the Council)

RICHARD B. PILCHER,30, Bloomsbury Square, London, W.C., Registrar and Secretary.
27th October, 1904.

The Book of Regulations for the Admission of Students, Associates, and Fellows may be obtained on application to Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C. Price One Shilling.

PLATINUM UTENSILS, SCRAP,
LAMP-ENDS, &c.,

Purchased at highest prices by—

DERBY & CO., LTD., 44, CLERKENWELL ROAD, LONDON.
N.B.—Platinum Sold.**CHEMICALS, Pure and Commercial.**

For Scientific and Technical Purposes

Specialities: **ETHERS, CHLOROFORM.****POLGLASE & CO.,** Tyne Vale Chemical Works, Skippersburn-rd.,
NEWCASTLE-ON-TYNE.**OLD PLATINUM**

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and Purchased.

ENERGETIC AGENT wants to add the
REPRESENTATION

of a few more good Firms

FOR SWITZERLAND.

Please address, "Z.B. 9077," care of Rudolf Mosse, Zurich.

ZINC

Suitable for the **MARSH-BERZELIUS Test for ARSENIC,**
As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.Also **WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, SHOT, &c.**

THE CHEMICAL NEWS.

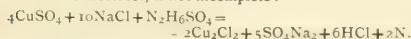
VOL. XC., No. 2347.

THE USE OF SULPHATE OF HYDRAZINE IN GASOMETRIC ANALYSIS.

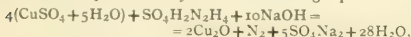
By J. DE GIRARD and A. DE SAPORTA.

GASOMETRIC analysis has the advantage of enabling us to make a certain number of the usual determinations with the aid of simple and commonly used apparatus with an accuracy quite sufficient for practical purposes. We thought it would be of advantage to extend the number of these determinations by taking advantage of the reducing powers of sulphate of hydrazine, and the regular disengagement of nitrogen which it effects in the cold with certain salts.

M. Purgotti (*Bull. Soc. Chim.*, Series 3, vol. xviii., p. 953) has already used sulphate of hydrazine for the estimation of salts of copper, but we have already pointed out that the following equation that he uses to show the reaction is incorrect, if not incomplete:—



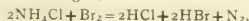
Actually, when we mix a solution of sulphate of hydrazine at 3 per cent, with a solution of sulphate of copper at 3.5 per cent, we obtain a crystalline blue compound, very slightly soluble, which separates out readily. This is a double sulphate of copper and hydrazine, $\text{SO}_4\text{Cu} \cdot \text{SO}_4\text{H}_2\text{N}_2\text{H}_4$. The previous addition of a concentrated solution of chloride of sodium does not prevent the formation of this salt, neither does cold affect its formation, but it is destroyed immediately, with the formation of cuprous oxide and the evolution of nitrogen, on the addition of soda-lye to the solution. Thus the intervention of sea salt is of no use, and, on the other hand, the presence of soda is indispensable for the reaction to take place in the cold; that is to say, under the conditions necessary for carrying out volumetric analyses. The reaction corresponds exactly with the following equation:—



so that 4 molecules of crystallised sulphate of copper weighing 998 set free 1 molecule of nitrogen weighing 28.

The operation succeeds very well with Trubert's calimeter, which can be easily obtained, and which we need not describe here.

The solution containing the salt of copper to be estimated is introduced into the apparatus with the solution of sulphate of hydrazine, and the flask is filled up to the gauge mark with soda-lye at 36° . It is best to react with small portions of soda on the mixture, and to surround the flask with cold water to prevent any increase of temperature. With 2 grms. of sulphate, dissolved in 30 to 50 c.c. of water, treated with 12 to 15 c.c. of a 3 per cent solution of sulphate of hydrazine, and about 20 c.c. of soda-lye, the latter being added drop by drop, we obtain an evolution of about 50 c.c. of gas, variable with the pressure and more especially with the temperature. Under the same conditions of temperature and pressure 0.214 gm. of chloride of ammonium treated with hypobromite ought to give the same volume of nitrogen,—



as is proved by experiment.

We have also observed (Second Supplement of Wurtz, No. 45, p. 250) the reduction of Fehling's solution by sulphate of hydrazine.

We thought we might apply this chemical reaction to the gasometric estimation of glucose, but we found that in this

case sulphate of hydrazine does not give off nitrogen in the cold, even in the presence of a large excess of caustic soda. On the other hand, if we apply heat the reduction becomes more advanced, and it is metallic copper that separates out.

Nevertheless, we are still able to apply the use of sulphate of hydrazine to the gasometric estimation of glucose. For this purpose we commence by reacting under the ordinary conditions of concentration, with a measured volume of the sugar solution on an excess of Pasteur's solution kept for some time at the boiling point. The boiling solution is thrown on to a filter, the cuprous oxide formed is washed with warm water, and re-dissolved in a few drops of a mixture of dilute nitric and sulphuric acids in boiling water. Thus we get back to the previous case (estimation of sulphate of copper). We may here remark that it is advisable to partially saturate the cupric liquor with an alkali, before acting on it in the cold with the sulphate of hydrazine and the soda.

We give the following results as an example; they were obtained at a temperature of about 20° and a pressure of 670 m.m.:—

0.200 gm. of glucose gave	..	40 c.c. nitrogen
0.300 " " "	..	60 " "
0.400 " " "	..	80 " "

Ten c.c. of grape-sugar syrup, treated with acetate of lead and sulphate of sodium, and diluted to 1 litre, giving 5.95 grms. of sugar by direct estimation with Fehling's solution (M. Bonnaux's method), gave 6.10 grms. of sugar by the gasometric method on two successive samples.

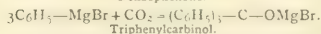
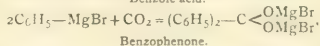
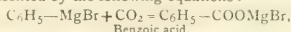
Although taking a little longer than Fehling's direct estimation, this method enables us to do away with the uncertainties of the final point of the reaction, and the personal errors which vary with the sensitiveness of the eye of the operator.

We can also employ sulphate of hydrazine for other gasometric estimations. We will only refer here to its direct action on nitrite of sodium. Five c.c. of a solution of hydrazine at 3 per cent, treated with 10 c.c. of a solution of nitrite of sodium at 3 per cent, gives off 29.5 c.c. of nitrogen in the cold, exactly the same volume as 5 c.c. of the same solution of sulphate of hydrazine decomposed by hypobromite of sodium, which corresponds to the equation, $2\text{NO}_2\text{Na} + \text{SO}_4\text{H}_2\text{N}_2\text{H}_4 = \text{N}_2 + \text{SO}_3\text{Na}_2 + 2\text{NOH} + 2\text{H}_2\text{O}$.

Thus hyponitrous acid is formed, which remains in solution and is decomposed when we raise the solution to boiling point, giving off protoxide of nitrogen.

Further, it is easy to prove directly the presence of this acid, for, if inversely, we treat nitrite of sodium with an excess of sulphate of hydrazine, the solution gives a yellowish-white precipitate with nitrate of silver. This precipitate when drained, detonates violently if heated on a strip of platinum-foil; it is therefore composed of hyponitrite of silver.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 15.

Action of Carbonic Acid on Phenylbromide of Magnesium.—G. Schreter.—The reaction of carbonic acid on phenylbromide of magnesium is fairly complex. Starting with 40 grms. of bromobenzene we obtain 1 gm. of diphenyl, only 2 grms. of benzoic acid, 2.5 grms. of benzophenone, 7 grms. of triphenylcarbinol, 1.5 grms. of a compound fusible at 165° , which seems to be a molecular compound of benzophenone and triphenylcarbinol. Further, there is a little phenol formed, through the action of the atmospheric oxygen. These reactions may be represented by the following equations:—



The relative quantities of these products vary with the experimental conditions.—*Berichte*, vol. xxxvi., p. 3005.

THE DETERMINATION OF LIME.

The gravimetric determination of calcium is almost invariably made by precipitating as oxalate and weighing as oxide or sulphate. The general practice is to precipitate from a slightly ammoniacal solution, which contains some ammonium chloride, by means of ammonium oxalate; and when pure solutions only are in question the results obtained are quite accurate, *e.g.* :—

CaO present. Grm.	CaO found. Grm.
0.0066	0.0067
0.0132	0.0131
0.0333	0.0332
0.0667	0.0670
0.1667	0.1669
0.3330	0.3345

If the lime is strongly ignited and weighed quickly the results agree very well with those obtained after moistening with sulphuric acid, re-igniting to low redness, re-weighing, and calculating from CaSO_4 to CaO. The ignited precipitate should be white, but if the ammonium oxalate contains manganese or the added ammonium chloride iron—as in my experience they may—the precipitates are slightly pink (and may even be brown), and to a corresponding extent heavier than they should be.

Lime is precipitated by little more than the theoretical amount of ammonium oxalate, but it is in no way detrimental to add large excesses, *e.g.* :—

Amount of ammonium oxalate (c.c.)	15	50	100
CaO precipitated (grm.)	0.1996	0.1996	0.1995

Lime may also be precipitated as oxalate from solutions containing free oxalic, citric, salicylic, or acetic acid, *e.g.*, when precipitated from a solution containing :—

20 per cent free acetic acid the CaO weighed	0.1992	grm.
8 " " " " " "	0.1985	"
2 " " " " " "	0.1990	"
0 " " " " " "	0.1993	"

In the absence of ammonium salts the precipitated calcium oxalate, even after boiling for some time, filters rather badly. The addition of acetic acid effects an improvement in this respect. In the presence of ammonium salts, however, the precipitates, if heated awhile, become distinctly crystalline, and filter and wash easily. The presence of ammonium salts does not otherwise affect the determination, *e.g.* :—

In the absence of ammonium salts the CaO weighed	Grm.
" presence of 20 grms. chloride	0.1996
" " " " nitrate	0.2000
" " " " acetate	0.2006
" " " " "	0.1990

If lime is being precipitated from solutions which contain other metallic salts it can generally be obtained in a purer form if an excess of free acetic acid is added than if the solution is kept neutral or made slightly alkaline, as many metallic oxides, with which calcium is commonly associated, are precipitated in alkaline solutions. The washing of the precipitate in the former case is then made with water containing about 1 per cent each of ammonium oxalate and acetic acid. The extent to which other metals may be present under these conditions has been studied experimentally. Unless otherwise stated, the following tests were carried out in solutions containing 8 per cent of free (B.P.) acetic acid and 2 decigrams. of lime.

When from 20 to 30 grms. of sodium or potassium chloride was present in the solution the results were from 1 to 3 per cent too high; the correct result can, of course, be obtained by re-precipitating.

Zinc, barium, and lead readily form insoluble compounds with ammonium oxalate; their presence would therefore always interfere with the determination of lime.

Nickel and cobalt are precipitated by ammonium oxalate after standing for some time, and must therefore always

be separated if more than comparatively small amounts are present.

Copper to the extent of a decigram. contaminates the lime only to a very slight extent or not at all, *e.g.*, 0.1987 grm. of CaO instead of 0.2000.

Aluminium (decigram.).—The solution should be neutralised with ammonia until a faint precipitate of aluminium hydrate appears; this should be cleared up entirely with a very slight excess of hydrochloric acid, and then 8 or 10 per cent of free acetic acid should be added. The slight excess of free hydrochloric acid must be destroyed by adding ammonium oxalate until the lime begins to be precipitated, and then in addition as much as will precipitate all the lime present. The CaO obtained under these conditions weighed 0.2000 grm., and was quite free from alumina.

Uranium shows no tendency to be precipitated with the lime, *e.g.*, 0.2002 grm. of CaO was obtained.

Arsenic also shows no tendency to be precipitated with the lime.

Molybdenum shows a slight tendency to be co-precipitated, but when a decigram. of this metal was present the CaO weighed only 0.2020.

Iron in the ferric state is not precipitated along with the lime to any serious extent; for example, 0.2031 grm. of CaO instead of 0.2000 grm. was obtained from a solution containing 0.1430 grm. of ferric oxide. Lime may also be precipitated directly from a solution of basic slag, according to both Immendorf and Reitmar, if the free hydrochloric acid in which it has been dissolved is neutralised with potassium or ammonium oxalate. The precipitated lime will be free from phosphoric acid, and contain traces only of other bases unless much manganese happens to be present.

Calcium phosphate is easily soluble in dilute acetic acid, and therefore the presence of phosphoric acid can interfere only to a very slight extent, *e.g.*, when precipitated from a solution containing 1 grm. of microcosmic salt, the CaO weighed 0.2008 instead of 0.2000 grm., and contained 0.0012 grm. of P_2O_5 .

Manganese, even when present in small amounts, is partly carried down with the lime. The separation of manganese from lime by means of bromine and ammonia is not exact, but it is often resorted to on account of its convenience. The manganese is more accurately separated by precipitating from a hot ammoniacal solution by means of sulphuretted hydrogen. There seems some uncertainty as to whether the separation by means of persulphates is accurate. It is often quite as convenient to neglect the presence of manganese until after the ignition, then to dissolve the impure lime in hydrochloric acid, evaporate the solution with sulphuric acid to fumes, and then determine the amount of the associated manganese by the bismuthate process, *e.g.* :—

0.2210 = weight of impure CaO.

0.0220 = weight of Mn_2O_4 determined by the bismuthate process.

0.1990 grm. CaO instead of 0.2000.

Chromium as a salt of chromic oxide exhibits no tendency to go down with the lime, but it prevents the precipitation of calcium oxalate to a serious extent however long the solution may be boiled. The results are, however, much better if a very large excess of ammonium oxalate is added, and the solution allowed to stand for several days. Chromium as chromic acid, however, exerts no influence on the precipitation except that, as it is reduced by oxalic acid in hot solutions, the entire precipitation must be carried out in the cold. The results are accurate.

Magnesia occurs more frequently than any other base in solutions from which lime has to be precipitated. The accurate precipitation of small amounts of lime from solutions containing comparatively large amounts of magnesia is a question of commercial importance, and makers of magnesia bricks, &c., for metallurgical purposes have often

good reason for complaining of the quantity of lime the analyst reports having found in their products. It is important to bear in mind that calcium oxalate is soluble in magnesium chloride, and that magnesium oxalate is only sparingly soluble in water. It is necessary, therefore, in order to ensure a complete precipitation of the lime, to add at least as much ammonium oxalate in excess as will transform all the magnesia into magnesium oxalate (i.e., about four times the weight of the magnesia present), and then to make the solution so dilute that no magnesium oxalate can crystallise out. The presence of free ammonia and warming of the solution favour the co-precipitation of magnesia; the presence of ammonium chloride retards it. The following method gives quite satisfactory results:—

Neutralise the solution, dilute it so that each 100 c.c. contains not more than 0.15 grm. of magnesia, add at least 10 grms. of ammonium chloride, and then acetic acid equal to 2 or 3 per cent of the volume of the solution, and, lastly, an amount of ammonium oxalate equal to four times the weight of the magnesia present, and as much besides as will precipitate the lime. Larger amounts of ammonium oxalate or ammonium chloride are without influence. The solution should be well stirred, but not heated, and allowed to stand for one hour or more before filtering. The following results were obtained with solutions which in each case contained 0.625 grm. of magnesia.

CaO added.	CaO found.
0.0133	0.0145
0.0133	0.0135
0.0333	0.0325
0.0660	0.0670

The first of these tests was allowed to stand twenty-four hours, the others stood only from one to two hours.

A.W.B.

AN IMPROVED FORM OF CONDENSER.

By HERBERT EDWARD BURGESS.

It will be admitted that a double surface condenser must necessarily be more efficient and economical than the ordinary Liebig or Graham type, but most condensers made on the double surface condensing system have serious disadvantages which militate to a great extent their usefulness and general adoption in laboratories. A few may be mentioned:—

1. Difficulty in cleaning.
2. In getting a uniform flow of water over the whole surface, which leads to considerable chances of breaking where the hot vapour meets the cold part of condenser.
3. When the outer condensing water is enclosed it entails the making of several sealed glass joints which are very liable to fracture, add to the cost of apparatus, and when broken cannot be repaired.

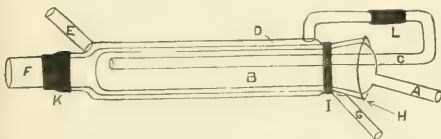


FIG. 1.

- A Cold water inlet to
- B Inner cold tube.
- C Outlet from ditto through
- D Rubber joint to
- E Outer cold-water jacket.
- F Outlet from ditto.

- F Condenser tube.
- G Outlet from ditto.
- H Ground joint.
- I and K Rubber joints.

4. They are all designed to be used in a vertical position, or if used in a horizontal position a small portion of the distillate will remain between the two condensing spaces.

To overcome some of these disadvantages I suggested to Messrs. C. E. Müller, Orme, and Co., Ltd., to make for me the condenser as shown in the illustration, and which I have found on the severest tests to be very efficient; it was primarily intended for distillations with direct steam, but answers equally well for ordinary distillations or under reduced pressure. It can be easily cleansed by removing the inner condensing tube; in case of breakage any part may be easily renewed at very small cost, or, in fact, can be replaced from the stores of any ordinary laboratory, or it may be used in any position with or without vacuum; it takes less than one-third of bench room than an ordinary Liebig type condenser.

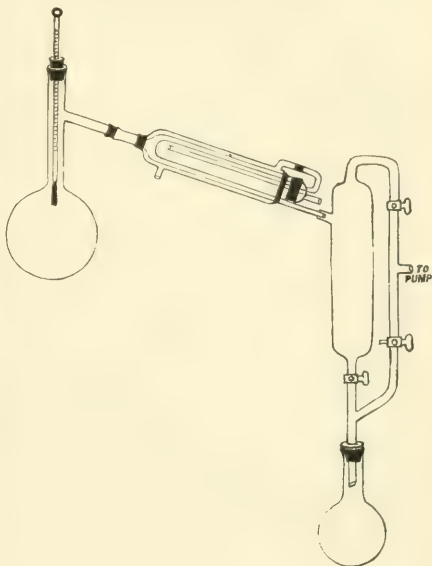


FIG. 2.

For distillations under reduced pressure, where fractions have to be separated, the fractionating end as shown in Fig. 2 will be found extremely useful and convenient.

Laboratories, London Essence Co.,
George Street, Camberwell, S.E.

Gummed Reagent Labels.—Messrs. F. E. Becker and Co. (W. and J. George, Ltd., Successors), of 23–27, Hutton Wall, E.C., have just issued a new assortment of gummed reagent labels that is rather out of the ordinary. The design of book has for its object the combination of “maximum usefulness with minimum waste.” The novelty consists in arranging the type and boundary lines of uniform size, so that parts of different labels can be joined together. In this way any possible—or, for that matter, impossible—combination of metal and acid radical can be built up; if the cutting and joining is done neatly it need scarcely be visible. The advantage of such an arrangement is obvious. The type is large and plain, and the book includes small labels for Pure, Commercial, Normal, Decinormal, &c.; also a number of large ones for drawers and shelves. They appear to be well gummed, and will be very useful in technical and college laboratories.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

THE Council of the Royal Society have made the following awards of Medals for this year :—

The Copley Medal to Sir William Crookes, F.R.S., for his long-continued researches in spectroscopic chemistry, on electrical and mechanical phenomena in highly rarefied gases, on radio-active phenomena, and other subjects.

The Rumford Medal to Professor Ernest Rutherford, F.R.S., for his researches on radio-activity, particularly for his discovery of the existence and properties of the gaseous emanations from radio-active bodies.

A Royal Medal to Professor William Burnside, F.R.S., for his researches in mathematics, particularly in the theory of groups.

A Royal Medal to Colonel David Bruce, R.A.M.C., F.R.S., for his researches in the pathology of Malta fever, nagana, and sleeping sickness, and especially for his discoveries as regards the exact causes of these diseases.

The Davy Medal to Professor William Henry Perkin, jun., F.R.S., for his discoveries in organic chemistry.

The Darwin Medal to Mr. William Bateson, F.R.S., for his contributions to the theory of organic evolution by his researches on variation and heredity.

The Sylvester Medal to Professor Georg Cantor, for his researches in the theories of aggregates and of sets of points of the arithmetic continuum, of transfinite numbers, and Fourier's series.

The Hughes Medal to Sir Joseph Wilson Swan, F.R.S., for his invention of the electric incandescent lamp and various improvements in the practical applications of electricity.

CHEMICAL SOCIETY.

The following are abstracts of papers received during the vacation and published or passed for publication in the *Transactions* :—

137. "The Action of Chromyl Chloride on Stilbene, Styrene, and Phenanthrene." By GEORGE GERALD HENDERSON and THOMAS GRAY.

Each of the hydrocarbons, stilbene, styrene, and phenanthrene, when treated with chromyl chloride in carbon disulphide solution, yields a solid brown additive compound. These solids are decomposed by water, and oxidation products of the hydrocarbons are liberated. Stilbene is oxidised to benzil, and, with partial decomposition, to benzophenone and benzaldehyde. Styrene yields benzaldehyde as the chief product, together with a trace of phenylacetaldehyde and a small amount of a chlorinated compound. The sole product obtained from phenanthrene was phenanthraquinone.

138. "The Stereoisomeric Tetramethyl Methylglucosides and Tetramethyl Glucose." By THOMAS PURDIE and JAMES COLQUHOUN IRVINE.

The pentamethyl glucose (m. p. 42–43°) obtained from tetramethylglucose, either by the silver oxide method of alkylation or by the action of methyl alcohol containing hydrogen chloride (*Trans.*, 1903, lxxxiii., 1035), proves to be tetramethyl- β -methylglucoside; the stereoisomeric liquid α -glucoside is produced simultaneously, but in much smaller proportion. The β -glucoside is characterised by its levorotatory power, its more rapid hydrolysis by hydrochloric acid, and its susceptibility to the hydrolytic action of emulsin.

In aqueous solution, tetramethyl glucose, like glucose itself, exhibits phenomena of mutarotation. The α -form (m. p. 88–89°); $[\alpha]_D^{20} + 100.8^\circ$ is obtained by repeated crystallisation of the crude aldose from petroleum; the β -form (Tanret's γ -form), or at least a mixture containing

a large excess of it ($[\alpha]_D^{20} 73.1^\circ$), is produced by heating the α -form above its melting-point. The modification, which is stable in solution ($[\alpha]_D^{20} 83.3^\circ$), is apparently a mixture of the two dynamic isomerides. In the solid state, the β -isomeride reverts to the α -form.

Mutarotation was also observed in benzene and carbon-tetrachloride, and therefore neither ionisation nor the formation of hydrates or compounds of the acetal class is essential for the occurrence of this phenomenon.

139. "The Alkylation of Galactose." By JAMES COLQUHOUN IRVINE and ADAM CAMERON.

The silver oxide method of alkylation, when applied to α -methylgalactoside, gives rise to tetramethyl α -methylgalactoside, a colourless, refractive liquid (b. p. 136–137°/11 m.m., $[\alpha]_D^{20}$ of the pure liquid is $+105.7^\circ$, and in aqueous solution $[\alpha]_D^{20}$ is $+143.4^\circ$). Hydrolysis with hot dilute hydrochloric acid leads to the production of tetramethyl galactose, a colourless refractive syrup (b. p. 172°/13 m.m.). After distillation, the alkylated sugar displays mutarotation, not only in water, but also in alcohol and benzene, the permanent values for these three solvents being $+109.5^\circ$, 62.6° , 90.0° respectively. In other respects, also, the behaviour of the compound supports the view that it has an oxidic structure.

When the substance is either heated with methyl alcohol and hydrochloric acid or treated with silver oxide and methyl iodide, the stereoisomeric tetramethyl α - and β -methylgalactosides are produced, the latter method giving a large excess of the β -compound, whilst the former yields a greater proportion of the α -isomeride. The crystalline β -form (m. p. 44–45°) is much more readily hydrolysed than its isomeride, either by dilute acids or by emulsin.

140. "A Method for the Rapid Ultimate Analysis of Certain Organic Compounds." By JOHN NORMAN COLLIE.

The method consists in burning the substance in a known volume of oxygen, noticing any change in the volume of the gas, and then, by absorbing the carbon diox. e' produced, data sufficient for the calculation of the per cent amounts of carbon and hydrogen are obtained.

Only those substances can be estimated which are not appreciably volatile in a vacuum, and which contain only carbon and hydrogen or carbon, hydrogen, and oxygen. The time required for an analysis is only about an hour; the amount of substance used can be reduced to nearly one-tenth of that ordinarily employed, and as the measurements depend on volumes of gases the method is very accurate.

141. "The Comparative Nitrifying Power of Soils." By SYDNEY FRANCIS ASHEY.

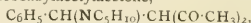
The method devised for comparing quantitatively the power of cultivated soils to convert their ammonia into nitrites and nitrates has justified itself by :—

1. Yielding samples giving reasonably similar nitrifying power from different parts of the same field.
2. Causing equal seedlings from the same sample to show similar nitrifying power.
3. Minimising loss of nitrogen by volatilisation of ammonia and denitrification during incubation.
4. Limiting the incubation period to about thirty days.
5. Showing a nitrifying power of the soils tested which corresponds with their fertility as gauged from manuring and crop production.

142. "The Action of Organic Bases on Olefinic Ketonic Compounds." By SIEGFRIED RUHEMANN and EDWIN ROY WATSON.

Benzylidenecacetylacetone readily unites with *m*-toluidine, *p*-toluidine, *m*-chloroaniline, *p*-chloroaniline, β -naphthylamine, and piperidine, but it does not combine with *o*-toluidine, α -naphthylamine, or tetrahydroquinoline.

Piperidinobenzylidenecacetylacetone, —



is stable in a dry atmosphere, but in the presence of moisture it gradually decomposes with the formation of enzyldenebisacetylacetone, benzaldehyde, and piperidine.

The production of benzylidenesacetylacetone and similar compounds from benzaldehyde and ketonic compounds is therefore preceded by the formation of additive compounds of piperidine with olefinic ketonic compounds. This view is supported by the fact that benzylidenesacetylacetone, which combines with piperidine, also condenses with acetylacetone in the presence of the base to form benzylidenesacetylacetone, whilst no such reaction takes place if tetrahydroquinoline, which does not form an additive compound with the olefinic ketone, is used instead of piperidine.

With phenylhydrazine, dibenzylidenesacetylacetone forms the phenylhydrazone, $(C_6H_5.CH:CH)_2C:N:NH.C_6H_5$, and not an additive compound; with ammonia, it yields a mixture of substances from which has been isolated the compound having the formula $C_{34}H_{35}N_3$.

Benzylidenesacetylacetone dibromide, when condensed with ammonia, yields aminobenzylidenesacetylacetone, $C_6H_5.C(NH_2):CH.CO.C_6H_5$; it therefore follows that the corresponding compound obtained by Wieland (*Ber.*, 1894, xxvii., 1150) from ammonia and *p*-nitrobenzylidenesacetylacetone dibromide is also unimolecular.

143. "Halides of the Acridines and Naphthacridines." By ALFRED SENIER and PERCY CORLETT AUSTIN.

The halogens combine directly with the acridines, forming a series of well-defined crystalline compounds, which are sparingly soluble in organic media, and are obtained by mixing the reagents either alone or in a suitable solvent. The products, which have characteristic colours, are unstable, especially in presence of water. The fluorescence, when in solution, which is so marked a character of acridines generally, and which depends on the presence of the acridine "fluorophore," is absent, except in three instances.

That these compounds are not substitution derivatives follows from their instability, the small number of halogen atoms which they contain, and the fact that no acridone is formed when they are treated with water or alkalis. They are therefore additive compounds, namely, halides. Moreover, the addition takes place in the acridine ring, for, were it otherwise, monadic atoms would be added only in pairs, which, however, is not the case, and a higher number would combine owing to the disruption of the centric benzene linkings.

Adopting this view, two formulæ are possible for the dihalides. The first, which is of the type of the dihydrides or dihydroacridines (Bernthsen and Bender, *Ber.*, 1883, xviii., 1802), is suggested for the non-fluorescent dihalides, and the second corresponding with the acridinium salts, alkylhalides, and alkylhydroxides, is employed for the dihalides which exhibit fluorescence. In accordance with the foregoing hypothesis, the tetrahalides should have formulæ of the former non-fluorescent type, and acridine tetrabromide, the only tetrahalide described, was found to be non-fluorescent.

Those compounds which contain one halogen atom combined with one and three molecular proportions of base respectively are regarded as being products intermediate between the bases and the dihalides, in the one case, and the dihalides and tetrahalides in the other, and to these products dimolecular formulæ are assigned.

144. "Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds. Part II. Cyanohydrins regarded as Complex Acids." By ARTHUR LAPWORTH.

Under certain conditions, an aqueous solution of potassium cyanide readily dissolves benzaldehyde and camphorquinone. From the resulting liquids, crystalline additive products having approximately the compositions $C_7H_6O.KCN.2\frac{1}{2}H_2O$ and $C_{10}H_{14}O_2.KCN.3H_2O$ have been isolated. These substances behave as salts of the corresponding cyanohydrins, which are probably much feeble acids than hydrocyanic acid itself.

145. "Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds. Part III. Action of

Potassium Cyanide on Mesityl Oxide." By ARTHUR LAPWORTH.

It was shown that when mesityl oxide is heated with potassium cyanide dissolved in dilute alcohol, hydrogen cyanide is first assumed at the ethylenic carbon linking, and that the potassium hydroxide which is simultaneously produced converts the product into mesitonic acid; more prolonged heating results in the formation of mesitylic acid, which necessitates the addition of a second molecule of hydrogen cyanide in this case to the carbonyl group, and the subsequent hydrolysis of the product.

146. "6-Aminocoumarin." By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

6-Aminocoumarin, although resembling the naphthylamines in containing two unsaturated rings, nevertheless behaves towards diazonium salts like a para-substituted benzenoid amine, giving rise to stable diazoamino-derivatives.

This base and its mono- and di-alkylated compounds and the corresponding hydrazine and diazocyanide are all coloured substances, whereas the salts of these bases, the acyl derivatives of the primary and secondary amines, the nitrosamines of the monoalkyl derivatives, the diazonium salts of the parent base and its quaternary bromides and iodides are colourless.

147. "Studies in Asymmetric Synthesis. I. Reduction of Menthyl Benzoylformate. II. Action of Magnesium Alkyl Haloids on Menthyl Benzoylformate." By ALEXANDER MCKENZIE.

When *l*-menthyl *dl*-mandelate is hydrolysed by an amount of potassium hydroxide insufficient for complete hydrolysis, an optically active mandelic acid is invariably obtained from the potassium salt thus formed. The mixture of esters remaining after this partial hydrolysis, when completely hydrolysed, yields mandelic acid which is either optically active or inactive, according to the experimental conditions. In the complete hydrolysis, by potassium hydroxide, of a mixture of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate containing an excess of either of those esters, racemisation phenomena are observed.

On reducing menthyl benzoylformate to menthyl mandelate and hydrolysing the latter, the mandelic acid obtained was inactive. But it does not follow from this result that equal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate were present in the product obtained by the reduction of menthyl benzoylformate, since, even if unequal amounts have been present, the mandelic acid obtained might still have been inactive owing to the racemising effect of the hydrolysing alkali.

Further investigation showed that a slight excess of *l*-menthyl *l*-mandelate was present in the reduction product, which, however, on hydrolysis, yielded *r*-mandelic acid.

When menthyl benzoylformate, $PhCO.CO_2.C_{10}H_{19}$, is acted on by magnesium methyl iodide and the magnesium addition compound then decomposed by water and dilute acid, a new asymmetric carbon atom is produced. In this instance, no racemising effects are observed on hydrolysing the product with alkali, since an optically active potassium salt is present in solution after the complete removal of the *l*-menthol, and this salt yields an optically active phenylmethylglycollic acid, $CMePh(OH).CO_2H$. An optically active phenylethylglycollic acid was also obtained in a similar manner.

That the optical activity exhibited by phenylmethylglycollic and phenylethylglycollic acids, prepared by Grignard's reaction, was actually due to their asymmetric synthesis was shown by preparing diphenylglycollic (benzilic) acid from menthyl benzoylformate and magnesium phenyl bromide. In this case, where a new asymmetric carbon atom was not produced, the resulting acid was inactive.

148. "The Relation of Position Isomerism to Optical Activity. II. The Rotation of the Menthyl Esters of the

Isomeric Chlorobromobenzoic Acids." By JULIUS BEREND COHEN and HENRY STANLEY RAPER.

The authors have extended the research of Briggs and Cohen on the relation of position isomerism to the rotations of the menthyl esters of the six dichlorobenzoic acids (*Trans.*, 1903, lxxxiii., 1213) by preparing and examining the menthyl esters of the ten isomeric chlorobromobenzoic acids.

The molecular rotations of these esters agree in a very satisfactory way with those of the dichlorobenzoic esters.

The greatest effect in decreasing the rotation is produced when the halogen enters the ortho-position with respect to the ester group; the least when both halogens are in the meta-position. The mean order of magnitude, beginning with the ester of lowest rotation, is as follows:—

2 : 6 ; 2 : 3 ; 2 : 5 ; 2 : 4 ; 3 : 4 ; 3 : 5 ; phenyl,

which is precisely the order of rotation of the dichlorobenzoic esters.

When the chlorine is nearer to the ester group than the bromine, a greater depression in the rotation is produced than by the reverse arrangement. Moreover, when the chlorine occupies the ortho-position to the ester group, the rotation is lower than that of the corresponding dichlorobenzoic ester. The general effect of bromine is to influence the rotation less than the chlorine—a result which seems to follow from the effect of the monohalogen esters.

The great contrast afforded by the two symmetrical compounds of both series, namely, the 3 : 5- and 2 : 6-esters, is not a little remarkable, and these isomerides may be regarded as the first and last terms of a series in which the 2 : 6-compounds have a high melting-point and low rotation, whilst the 3 : 5-isomerides have a low melting-point, low density, and high rotation.

149. "The Relation of Position Isomerism to Optical Activity. III. The Rotation of the Menthyl Esters of the Isomeric Iodobenzoic Acids." By JULIUS BEREND COHEN and HENRY STANLEY RAPER.

In a former communication (Cohen and Briggs, *Trans.*, 1903, lxxxiii., 1216), the rotations of the menthyl esters of the three monochlorobenzoic acids were given and compared with the constants obtained for the monobromobenzoic esters by Tschugaeff. The authors have now determined the constants for the menthyl esters of the three iodobenzoic acids.

150. "The Chlorination of the Trichlorotoluenes in presence of the Aluminium-mercury Couple. The Constitution of the Tetrachlorotoluenes." (Part V.). By JULIUS BEREND COHEN and HENRY DRYSDALE DAKIN.

In previous papers (Part III., *Trans.*, 1901, lxxix., 1111; Part IV., *Trans.*, 1902, lxxxi., 1325), the authors have traced the progressive chlorination of toluene as far as the formation of the trichlorotoluenes. The products formed on introducing a fourth chlorine atom into each of the six trichlorotoluenes have now been investigated.

On chlorinating 3 : 4 : 5-trichlorotoluene at 0°, the chlorine enters the side-chain instead of the nucleus.

Although there appears to be no general law determining the position of the fourth entrant chlorine atom, yet there exists a remarkable agreement between the positions taken by the entrant chlorine atoms and nitro-groups when the first two chlorine atoms have been introduced into either benzene or toluene. Whatever the ultimate explanation may be, it is clear that after the first two chlorine atoms have been introduced into benzene and toluene the special rules which usually govern substitution are wholly or in part set aside in favour of a more general law which includes both the substituent chlorine atom and also the nitro-group.

151. "The Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds. Part I. Alkyl Haloids." By ARTHUR SLATOR.

The reactions between sodium thiosulphate and methyl, ethyl, and ethylene haloids have been investigated in dilute solution, and shown to be in most cases bimolecular, thus,

$\text{CR}_3\text{I} + \text{S}_2\text{O}_3^{--} = \text{CR}_3\text{S}_2\text{O}_3^{--} + \text{I}^+$. Water was used as a solvent whenever possible, but in a few cases a mixture of this liquid and alcohol had to be employed.

The rate of reaction is approximately trebled for a rise of 10°. The velocity-coefficients may be used to compare the reactivities of these haloids. With two of the compounds ($\text{C}_2\text{H}_5\text{I}$, $\text{C}_2\text{H}_5\text{BrCl}$) the velocity of the reaction with excess of thiosulphate is independent of this excess, and the reaction is therefore unimolecular. To explain this result, it is suggested that the haloids are capable of existing in two tautomeric forms, and that the measurable reaction represents the change of one form into the other.

152. "Note on Methyl Fluoride." By JOHN NORMAN COLLIE.

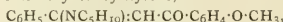
Methyl fluoride under 2 m.m. pressure, when contained in a vacuum tube having aluminium electrodes and subjected to the spark from an induction coil, gives a bluish green colour. The spectrum, however, rapidly changes, and the characteristic lines of hydrogen make their appearance. When sparked under the ordinary pressure, the gas is almost immediately decomposed in the following manner:— $4\text{CH}_3\text{F} = 4\text{C} + 2\text{H}_2 + 2\text{H}_2\text{F}_2$. In glass tubes, a secondary change occurs; the silicon fluoride formed by the action of the hydrogen fluoride on the glass is reduced by the hydrogen, and silicon is deposited:— $\text{SiF}_4 + 2\text{H}_2 = 2\text{H}_2\text{F}_2 + \text{Si}$.

153. "Acetylenic Ketones." By EDWIN ROY WATSON. The action of various bases on bromobenzylideneacetophenone, $\text{C}_6\text{H}_5\text{CBr}:\text{CH}:\text{CO}:\text{C}_6\text{H}_5$, has been investigated in the hope that a molecule of hydrogen bromide might thereby be eliminated from this compound (compare Ruhemann and Watson, *Trans.*, 1904, lxxxv., 457). The action of solid powdered potash gives rise to phenylacetylene, potassium benzoate, and potassium bromide.

The action of alcoholic ammonia gives rise to aminobenzylideneacetophenone, $\text{C}_6\text{H}_5\text{C}(\text{NH}_2):\text{CH}:\text{CO}:\text{C}_6\text{H}_5$, and by the action of piperidine two compounds—dipiperidinobenzylideneacetophenone and piperidinobenzylideneacetophenone—are produced. Strong bases replace the bromine atom in bromobenzylideneacetophenone by an amino- or substituted amino-group.

Phenylpropyl chloride reacts readily with anisole to produce the expected acetylenic ketone, methoxybenzylphenylacetylene. On substituting benzene for anisole the simple reaction no longer occurs, but several substances are produced, including a hydrocarbon having the empirical formula $\text{C}_{14}\text{H}_{12}$.

Methoxybenzylphenylacetylene and piperidine yield piperidinomethoxybenzylstyrene,—



whilst the action of hydroxylamine gives rise to 1-phenyl-3-methoxyphenylisooxazole.

Benzoylphenylacetylene yields the phenylhydrazone, $\text{C}_6\text{H}_5\text{C}:\text{C}(\text{C}_6\text{H}_5):\text{N}:\text{NH}:\text{C}_6\text{H}_5$, and the anilino benzoylstyrene, $\text{C}_6\text{H}_5\text{C}(\text{NH}:\text{C}_6\text{H}_5):\text{CH}:\text{CO}:\text{C}_6\text{H}_5$, when treated with phenylhydrazine and aniline respectively.

154. "Note on Bergamot Oil and Other Oils of the Citrus Series." By HERBERT EDWARD BURGESS and THEODORE HENRY PAGE.

Acetic acid, octylene, pinene, camphene, and limene have been identified as constituents of a specimen of pure oil of bergamot. The pungency of the first fractions of this oil on distillation is accounted for by the acetic acid, which was also found in smaller quantities in lemon oil, and is probably present in the other oils of this series.

The octylene found in lemon oil was identical with that in bergamot oil, for both gave butyric acid on oxidation with potassium permanganate. It is probably a normal constituent of the citrus oils. A second phenylurethane isolated from the terpineol fraction of distilled oil of limes melts at 132°, is more soluble than that obtained from ordinary terpineol, crystallises in tufts of needles, and gives on hydrolysis an oil with an intense odour of distilled oil of limes.

155. "The Resolution of Externally Compensated Dihydro- α -methylindole." By WILLIAM JACKSON POPE and GEORGE CLARKE, jun.

On crystallising externally compensated dihydro- α -methylindole with *d*-bromocamphorsulphonic acid, *l*-dihydro- α -methylindole *d*-bromocamphorsulphonate, $C_{10}H_{11}N \cdot C_{10}H_{11}Br \cdot SO_3H$, first separates, and on purification crystallises in needles (m. p. $179.5-180.5^\circ$; $[M]_D + 27.8^\circ$ in aqueous solution). With caustic soda it yields *l*-dihydro- α -methylindole, which is obtained as a colourless oil (b. p. $22.8-22.9^\circ$; $[a]_D - 13.61^\circ$ in a 1 dm. tube). The base is dextrorotatory in ethyl alcohol and benzene solutions, but levorotatory in ethereal solution.

A more sparingly soluble dihydro- α -methylindole *d*-bromocamphorsulphonate (m. p. $124-125^\circ$) accompanies the above salt, but, although it has the low molecular rotatory power of $[M]_D + 24.62^\circ$ in aqueous solution, corresponding with the presence of a basic ion of $[M]_D - 30^\circ$, this salt yields inactive base and inactive benzoyl and acetyl derivatives.

On adding caustic soda to the final mother-liquors obtained during the resolution, impure *d*-dihydro- α -methylindole separates, but was not obtained free from the *l*-isomeride; its benzoyl and acetyl derivatives were, however, prepared in a state of purity, and have properties corresponding with those of their optical antipodes.

156. "The Vapour Pressures of Sulphuric Acid Solutions and the Molecular Condition of Sulphuric Acid in Concentrated Solution." By BRYCE CHUDLEIGH BURT.

The vapour pressures of sulphuric acid solutions of various concentrations (from 25 to 95 per cent H_2SO_4) have been determined by an ebullioscopic method. The values so obtained lie on smooth curves when plotted against temperature and concentration. The molecular weight has been calculated from Raoult's corrected formula:—

$$m = M \cdot \frac{g}{G} \cdot \frac{p'}{p - p'}$$

where m = molecular weight of solute; M = molecular weight of solvent in the gaseous state; g = weight of solute; G = weight of solvent; p = vapour pressure of pure solvent; p' = vapour pressure of solution. The values for m obtained vary over very wide limits, increasing with rise of temperature and decreasing with increase in concentration. The different values do not lie on smooth curves when plotted against temperature and concentration.

These abnormalities can only be explained by supposing that combination occurs between the solvent and solute with the formation of complex molecules, the formation of such complexes being favoured by an increase in concentration, but not by a rise in temperature.

157. "Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds. Part IV. Addition of Hydrogen Cyanide to Benzylidenacetophenone." By ARCHIE CECIL OSBORN HANN and ARTHUR LAPWORTH.

The addition of hydrogen cyanide to benzylidenacetophenone takes place only in presence of a considerable quantity of potassium cyanide, and the failure of Rupe and Schneide (*Ber.*, 1895, xxviii., 957) to bring about the addition process is thus explained. When the solution is but feebly alkaline, the product is β -benzoyl- α -phenylpropionitrile, $CHPh(CN) \cdot CH_2 \cdot C(=O)Ph$, but in presence of alkali the latter condenses with unaltered benzylidenacetophenone to yield the compound $C_{17}H_{15}ON$, which Rupe and Schneide obtained in small quantities.

The *orime*, $CHPh(CO_2H) \cdot CH_2 \cdot C(=O)Ph \cdot N \cdot OH$, when warmed with sulphuric acid, undergoes the Beckmann change, yielding phenylsuccinic acid and aniline, by which reaction the constitution of the ketonic acid is established.

By means of the quinine salt, β -benzoyl- α -phenylpropionic acid was resolved into its optical isomerides; the *laevo*-acid, melting at $176-178^\circ$ in 6 per cent ethyl acetate solution, had $[a]_D - 157.57^\circ$, whilst the *dextro*-acid had $[a]_D + 157.3^\circ$.

158. "The Bromination of Silver Cyanate." By GEORGE DEAN.

Silver cyanate, when treated with an equivalent weight of bromine in a sealed tube, yielded a yellow product, $AgCNBr$. The substance, which did not darken on exposure to light, gave off bromine when heated above 70° . At $300-400^\circ$, the bromine evolved from the substance was accompanied by a thick sublimate of cyanogen bromide. The substance dissociated under $10-20$ m.m. pressure. Water acts on the compound, yielding silver bromide, cyanuric acid, carbon dioxide, and nitrogen; hydrochloric acid gives rise to a mixture of silver chloride and bromide, whilst cyanogen chloride, bromine, and oxygen are eliminated. The compound oxidises alcohol to acetaldehyde. When the cyanate was brominated at a lower temperature, much more halogen was absorbed; the product, however, was readily decomposed in a current of air, leaving the less brominated compound.

159. "The Decomposition of Chloral Hydrate by Sodium Hydroxide and by certain Salts." By EMIL ALPHONSE WERNER.

It is shown that the quantity of chloral hydrate decomposed by sodium hydroxide is a function of the temperature, for one molecular proportion of this alkali is capable of decomposing from one to four molecular proportions of the hydrate with production of chloroform, sodium formate, and free formic acid. Sodium acetate and similar salts are also capable of decomposing the hydrate with the production of formic acid. Water and dilute acids do not decompose chloral hydrate in this manner.

Two alternative theories are put forward to explain the decomposition. Firstly, it is assumed that a sodium derivative, $CCl_3 \cdot CH(ONa) \cdot OH$, formed on adding the alkali or salt, is immediately decomposed into chloroform and sodium formate. The decomposition of relatively large proportions of the hydrate by sodium hydroxide is easily explained in this way.

Secondly, the production of "nascent" carbon monoxide, $>C:O$, as distinct from C_2O , is suggested, this hypothetical substance then uniting with water to give formic acid.

160. "Contributions to the History of Glyoxylic Acid." By HEINRICH DEBUS.

Two views still prevail with regard to the formula of glyoxylic acid; some chemists represent its composition by the formula $C_2H_2O_3 \cdot H_2O$, whilst others prefer the expression $C_2H_4O_4$. The author, after discussing the arguments in favour of each formula, comes to the conclusion that the formula $C_2H_2O_3 \cdot H_2O$ is more in harmony with the properties of glyoxylic acid than the other.

Some basic salts of glyoxylic acid are described which readily decompose into the corresponding glycolates and oxalates.

161. "The Colouring Matters of the Stilbene Group." (1). By ARTHUR GEORGE GREEN.

The colouring matters of the stilbene class cannot have the simple structure assigned to them either by O. Fischer and Hepp, or by Bender and Schultz. Apart from the general improbability that substances so constituted would have dyeing properties, the following facts indicate that they have a more complex structure:—

1. Colouring matters can be obtained from *p*-nitro-toluenesulphonic acid by condensation with alkalis under suitable conditions, which, although having the general characteristics of Curcume S or Direct Yellow, contain aldehydic groups in addition to the stilbene group.

2. Stilbene dyes of mixed type can be obtained by condensing dinitrostilbenedisulphonic acid with aromatic amines under the influence of alkalis.

3. Curcume or Direct Yellow does not give rise on oxidation to dinitrostilbenedisulphonic acid, but furnishes a yellow dye of greener shade, which is very similar to the first product of the alkaline reduction of dinitrostilbenedisulphonic acid.

The author has endeavoured to elucidate the constitution

of the crimson-red compound, which invariably precedes the formation of the stilbene colouring matter, and is evidently the first phase of the condensation. The fact that this substance, on oxidation with hypochlorite, gives dinitrostilbenedisulphonic acid (Green and Wahl, *Ber.*, 1897, xxx., 3097), and is again regenerated from this acid on reduction, supported by a study of its phenyl ester and the analogous chloro-compound (compare next abstract), leads to the view that the crimson-red intermediate compound is a nitroso-stilbene or stilbene nitrolic acid having a quinonoid structure in alkaline solution.

102. "The Colouring Matters of the Stilbene Group." (II.). By ARTHUR GEORGE GREEN, FRED SCHOLEFIELD, and FRED MARSDEN.

In order to elucidate the constitution of the crimson-red compound obtained on heating *p*-nitrotoluenesulphonic acid with caustic alkalis, and which forms the first phase of the stilbene condensation, the authors have investigated the behaviour of the corresponding phenyl ester, $C_6H_3(CH_3)(SO_3C_6H_5)(NO_2)[1:2:4]$, and chloro-compound, $C_6H_3(CH_3)Cl(NO_2)[1:2:4]$. The first of these compounds, in alcoholic solution, gives, on adding caustic soda, an intense bright blue coloration even in the cold; the second gives a reddish-violet coloration at 20–30°.

It being found impracticable to isolate these coloured substances on account of their extreme instability, their behaviour on oxidation was studied. They are rapidly decolorised both by sodium hypochlorite and by air, and give rise to derivatives of dinitrostilbene. From the phenyl ester, a mixture of the *trans*- and *cis*-phenyl dinitrostilbenedisulphonates was produced. The same two compounds were also obtained from Green and Wahl's dinitrostilbenedisulphonic acid by conversion into the sulphonic chloride, and treatment with sodium phenoxide. This fact serves to confirm the constitution assigned above, and also shows that the dinitrostilbenedisulphonic acid, and probably also the crimson-red intermediate compound and the stilbene colouring matters generally, must consist of mixtures of *trans*- and *cis*-isomerides.

The reddish-violet intermediate compound from *o*-chloro-*p*-nitrotoluene, on oxidation with air or sodium hypochlorite, yielded a mixture of *trans*- and *cis*-dichlorodinitrostilbenes; the yield of the two isomerides being nearly theoretical, the formation of a third substance is excluded, and a simple connection between the coloured intermediate compound and the respective dinitrostilbene derivative is indicated. This is further supported by the fact that these dinitrostilbene derivatives are readily re-converted by alkaline reducing agents, such as phenylhydrazine and caustic soda, into the blue and reddish-violet compounds from which they are obtained. The authors are thus led to assign to the latter the structure of nitrostilbenes or stilbene nitrolic acids.

103. "Researches on Chromorganic Acids; the Behaviour of [Chromic Hydroxide towards Oxalic Acid and certain other Organic Acids." By EMIL ALPHONSE WERNER.

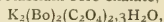
An aqueous solution of oxalic acid, when saturated with chromic hydroxide, yields a deep purplish-red liquid, which, on evaporation, leaves a dark green residue, appearing almost black by reflected light. This compound has the properties of a true chromoxalic acid, $H_7Cr_4(C_2O_4)_6(OH)_{5.4}H_2O$, and yields an ammonium salt, $(NH_4)_3Cr_4(C_2O_4)_6(OH)_{5.2}H_2O$.

Whilst thoroughly washed chromic hydroxide is readily dissolved by oxalic acid in the proportion required by the formula $Cr_2(C_2O_4)_3$, this is not the case with other related organic acids. Under similar conditions, malonic acid dissolves approximately 50 per cent of the calculated amount, whereas, with succinic acid, the interaction is appreciable. A chromomalonic acid, having the formula $H_7Cr_4(C_3H_2O_4)_6(OH)_5.6H_2O$, analogous to the chromoxalic acid, was obtained, and also a chromomalonnate, $K_2Cr_2(C_7H_2O_4)_4.10H_2O$, forming dark purplish-red crystals, the analogue of Croft's red chromoxalate.

The proportion of chromic hydroxide dissolved by malic, tartaric, tricarballic, citric, glycollic, and lactic acids

under the conditions described is relatively small, varying from a minimum of 12 per cent (malic acid) to a maximum of 27 per cent (lactic acid). In all these cases, chromorganic acids are produced, having, in general, properties resembling those of chromoxalic acid. With tartaric acid, a saline chromium tartrate, $Cr_2(C_4H_4O_6)_3$, is also formed. When the red salt, $K_2Cr_2(C_2O_4)_4.10H_2O$, is boiled in aqueous solution with 2 molecules of potassium oxalate, the blue chromoxalate, $K_6Cr_2(C_2O_4)_6.6H_2O$, is produced; a similar result is brought about by other salts, such as potassium acetate, malonate, or succinate, and so far no chromium compound containing two different acid groups has been obtained.

A well-defined potassium boro-oxalate,—



which is readily obtained by boiling solutions of potassium metaborate and oxalic acid or boric acid and potassium-hydrogen oxalate, is described. A similar compound is not formed with malonic or succinic acid.

(To be continued.)

NOTICES OF BOOKS

Imperial Institute. Technical Reports and Scientific Papers. Edited by WYNDHAM R. DUNSTAN, M.A., F.R.S. With a Preface by the late Sir FREDERICK ABEL, Bart., K.C.B., F.R.S. London: Richard Clay and Sons. 1903. Pp. 236.

THE technical reports and scientific papers included in this volume are selected from among the more important of those which have emanated from the Scientific and Technical Department of the Imperial Institute since it was established on a definite footing in 1896. The department has been very widely used by India and the Colonies for the purpose of ascertaining, chiefly through chemical investigation in its laboratories, the composition of raw materials of all kinds.

In many cases the results of these investigations have suggested possible uses for the products, suggestions which in many cases have been put to practical tests by manufacturers.

The technical reports cover a variety of subjects, such as minerals, including coal, iron ores, mica, &c., fibres, essential and edible oils, and oil seeds, rubber and gutta-percha, gums and resins, medicinal plants and tobacco, tanning and dyeing materials, fodder, timber, &c. The scientific papers have been chiefly communicated to the Royal and Chemical Societies, and the principal papers are here reprinted from the *Transactions and Proceedings* of these Societies. The appendix contains a paper on "The Coal Resources of India," which embodies a report originally made by Prof. Dunstan to the Government of India in 1898. The volume is a valuable one, containing as it does a large amount of information of great importance to India and the Colonies.

Tables for Qualitative Chemical Analysis. Arranged for the Use of Students. By A. LIVERSIDGE, M.A., LL.D., F.R.S., Hon. F.R.S.E., Associate of the Royal School of Mines, London, Professor of Chemistry in the University of Sydney. Second Edition. London: Macmillan and Co. 1904.

In these tables the attempt has been made to combine the advantages of quantitative methods with the process of qualitative analysis. The course includes some original and exceedingly valuable methods of working. The student is required to use weighed and very small quantities of materials, to promote accuracy of work and to save time. The advantage of the use of "equivalent solutions" is insisted upon. Much stress is laid upon the value of preliminary dry tests for minerals and common substances. The student who has been well grounded in this branch of

analysis, if provided with a blowpipe, a candle, and a few accessories and reagents, is almost independent of a laboratory.

The book begins with the reactions of metals, then acids, alcohols, and their derivatives, carbohydrates, glucosides, aromatic compounds, and alkaloids. Then follows a very complete set of "Tables for Qualitative Chemical Analysis."

There is also an Appendix with Tables of Solubilities, Reagents in Equivalent Solutions, International Atomic Weights, Weights and Measures, and Formulæ of Reagents.

Altogether the book is a useful thoroughly workable textbook, and one that is likely to find considerable favour with teachers of chemistry.

There is a complete index, and the price is very reasonable.

Percentage Tables for Elementary Analysis. By LEO F. GUTTMANN, Ph.D., A.C.G.I., A.I.C. London and New York: Whittaker and Co. 1904.

The tables are for the rapid calculation of the percentage of carbon and hydrogen in a substance which, on combustion, yields carbon dioxide and water, and are calculated for O=16.00, C=12.00, and H=1.01. The method of interpolation for the fourth place of decimals is accurate. The headings of all the tables are printed in German, French, and English, and there is also included a table for the reduction of volumes of nitrogen to grammes.

CORRESPONDENCE.

RADIUM.

To the Editor of the Chemical News.

SIR,—While there is so much being said in all the chemical and scientific journals of Europe and America regarding radium, it may be interesting to the scientific world to know something of the history and discovery of the ores that have given the world a new theme in mining to talk about. Before going into details, it may be said that the home of radium is in the uranium mines of the La Sal mountains in Utah, and nowhere else in the world is that character of ore being produced in sufficient quantity to supply the demand.

Early in 1888 M. Charles Polias, a French professor residing in Denver, went into the La Sal country in search of uranium deposits, stating that the supply from the uranium mines in Germany was gradually decreasing, and that a new field must be found to supply the demand. Professor Polias located several promising deposits along Rock Creek and Sinbad Valley, and, gathering up a few samples, returned to Paris for the purpose of determining the value of the mineral. It was found to contain values enough to warrant further investigation, and in 1890 a French company began the erection of a uranium plant near the deposits. But when the plant was nearly ready for operation the mill buildings caught fire and were destroyed, thus ending the explorations of Professor Polias and the French company.

In the year 1900, S. F. Lockwood, a New York capitalist, and William Banta, a young metallurgical student, secured an option on the Welsh-Loffitt group of uranium mines near Richardson, also in the La Sal mountains, and began to investigate the ore. They were engaged for a full year in thoroughly analysing this ore for the rare metal, outside of the ordinary mineral values. The ore was found to contain seven different metals, in addition to gold, silver, and copper. It was by pure accident that the radium values were discovered. Now during all this time the French chemists were ignorant of the source of the ore from which

they had discovered their radium, and were relying on the pitchblende products of the Hungarian mines for their small and limited supply.

Messrs. Lockwood and Banta organised a company to develop the property, and are building a reduction plant at Niagara Falls, New York, which will soon be completed, and immediately begin experimental work upon the ore. When it is satisfactorily known that their Niagara plant is a success, and just what kind of machinery and chemicals are required to work the ores, they will build a plant on the Grand River, two miles from the deposits, and thoroughly and systematically work the property. Mr. Lockwood is very sanguine in his belief that they are now prepared to successfully carry out their work, and that within a very short time they will be able to show the scientific world something that is new to the mining industry in general, and America in particular.

When radium, as a commercial metal, was discovered by Professor and Madame Curie in Paris in 1898, its value was quoted at something like £1,000,000 per pound, and only a grm. of the metal was on the market. The present price is about £560,000 per pound, but Mr. Lockwood confidently states that they will be able to reduce the value of this precious metal to about £125,000 per pound. It requires 2000 tons of the ore to be reduced to produce one pound of the radium ore.

The vein in which the ore is found is a true fissure, fully 40 feet wide, in a white sandstone formation. It has been exposed for 3000 feet by cuts and shafts, so the company will experience no lack of ore.

Hoping that the above may be of some interest and value to your readers,—I am, &c.,

H. OTLEY BEYER.

University of Denver,
Denver, Colorado.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxiv., No. 16, October 17, 1904.

The Boiling-point Constants of Mixtures.—C. Marie.—Experiments upon the boiling-points of mixtures of alcohol and water, in which resorcin was dissolved, do not verify the formula theoretically calculated by Nernst,

$$\frac{1}{K_m} \left(\frac{1}{K_1} \frac{q}{100} + \frac{1}{K_2} \frac{100-q}{100} \right);$$
 where K_1 , K_2 represent the molecular elevation of the two solvents, q and $100-q$ their relative proportion by weight, and K_m the boiling-point constant of the mixture. With four different mixtures of alcohol and water—

K_m (observed)	10.36	12.13	15.99	22.05
K_m (calculated)	9.36	7.39	6.80	6.36

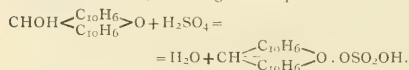
The author considers this divergence between observed and calculated results to be due to certain approximations made by Nernst in calculating his formula. Experiments were also made on mixtures of alcohol and water containing a solid soluble in one of the constituents, insoluble in the other, and partially soluble in the mixture. The addition of a solid—soluble in water, insoluble in alcohol—is found to lower the boiling-point of the mixture.

The Action of Magnesium Alkyl Compounds upon the Halogen Derivatives of Phosphorus, Arsenic, and Antimony.—N. Auger and M. Billy. —The object of these researches was to obtain mono- and di-alkyl derivatives of the metalloids of the trivalent group. The chloride of the metal was dissolved in anhydrous ether and cooled to a low temperature by means of solid carbon dioxide and

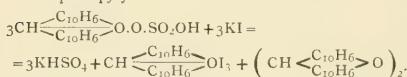
acetone. Magnesium ethyl (or methyl) bromide was then slowly added from a dropping funnel. Mono- and dialkyl derivatives were isolated from the products of the reaction. This treatment proved most successful in the case of antimony, a mono-ethyl iodide of which ($C_2H_5SbI_2$) was precipitated by means of excess of KI. This substance, when pure, consists of golden scales, which melt at 43° and are decomposed at 200° .

An Organic Persulphate.—R. Fosse and P. Bertrand.

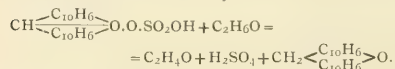
—When dinaphthopyranol, $C_{10}H_6 \begin{smallmatrix} \text{CHOH} \\ \text{O} \end{smallmatrix} C_{10}H_6$, or the oxide of dinaphthopyryl, $(C_{10}H_6 \begin{smallmatrix} \text{CHO} \\ \text{O} \end{smallmatrix} C_{10}H_6)_2O$, is added to dilute sulphuric acid and gently heated, a blood-red solution is produced, which, when filtered and cooled, crystallises into a red mass. The pyranol has reacted with one molecule of acid, according to the equation—



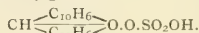
This sulphate has oxidising properties; when treated with KI the red solution is decolourised and pyryl tri-iodide and bis-dinaphthopyryl are formed:—



It transforms alcohol into aldehyde:—



These reactions make it evident that the graphic formula must be that already given, viz.,—



The Constitution of the Rosaniline Salts, and the Mechanism of their Formation.—Jules Schmidlen.—In a previous paper the two phases accompanying the solution of rosaniline carbinol in dilute acetic acid were described. The author ascribes these two phases to the intermediate formation of the colourless tetraoxycyclohexane rosaniline, which is unstable in weak acids. Hence the secondary phase, by which—with the loss of four molecules of water—the hexahydrobenzene nucleus is converted into a quinone nucleus and fuchsin is formed. The cyclohexane derivative is, however, stable in strong acids. Hence, when excess of acid is added to fuchsin, the rosaniline trichloride first formed (being unstable in solution) takes up four molecules of water, and is converted into the colourless stable tri-acid salt of tetracyclohexane rosaniline. When the carbinol is dissolved in excess of acid, the tri-acid cyclohexane derivative is formed at once, no secondary phenomenon being observed.

Tetrahydride and Octohydride of Anthracene.—Marcel Godchot.—The tetrahydride, $C_{14}H_{14}$, forms colourless crystals, which melt at 89° and can be sublimed. It is soluble in boiling benzene, and the solution has a blue fluorescence. It easily loses four atoms of hydrogen. The octohydride, $C_{14}H_{18}$, crystallises in little transparent and colourless tables; it melts at 91° , and sublimes above its melting-point. It dissolves in warm alcohol, acetic acid, benzene and its homologues. Its solutions have a characteristic green fluorescence. It combines with picric acid to form a crystalline picrate. Treated with bromine, a dibromo-octohydride of anthracene ($C_{14}H_{16}Br_2$) and a dibromohexahydride of anthracene ($C_{14}H_{14}Br_2$) are simultaneously formed. When the octohydride is oxidised, two new substances are produced—a tetrahydroanthraquinone and a hexahydroketone of anthracene.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xxxvii., No. 14, 1904.

Origin of Fusel Oils.—O. Emmerling.—Repeated experiments performed by the author, using different yeasts and carbohydrates, prove that, so long as the material is perfectly pure, fusel oils are either not produced at all, or else in only very minute quantities. Hence the formation of fusel oils is due to the action of bacteria upon the carbohydrates. This has been conclusively proved by many experiments. The author has not succeeded in isolating these bacteria, though he has repeatedly met with the same forms in fermentations. The most suitable materials for the formation of fusel oils appear to be starch and saccharose, especially if they have not been subjected to hydrolysis. As by-products of the reaction hydrogen and carbon dioxide are formed and also butyric acid. Pentoses also appear to be capable of giving rise to fusel oils. The examination on a small scale of the fusel oils obtained showed the presence of propyl, butyl, and amyl alcohol, and traces of ethyl alcohol. The time in which fermentation is completed varies very considerably; usually all the fusel oil is formed in four weeks, sometimes much sooner. In a few cases, for some unexplained reason, no higher alcohols whatever are formed.

Action of Light on Triphenylmethyl.—M. Gomberg and L. H. Cone.—If 3 per cent solutions of the different analogues of triphenylmethyl are kept for some time in absence of air, their colour gradually disappears, and at the same time the dissolved substances lose their unsaturated character. This was supposed to be caused by some unknown agent which had an effect similar to that of small quantities of hydrochloric acid, which convert the triphenylmethyl into hexaphenyl ethane. The authors have now shown that the cause of this phenomenon is the action of light. The analogues are apparently much more sensitive to light than the triphenylmethyl itself, and almost always lose their colour in two months (except in the case of solutions of naphthylidiphenylmethyl), while triphenylmethyl itself can be kept in diffused daylight for more than a year without suffering any appreciable decomposition. A solution of triphenylmethyl in benzene rapidly fades in direct sunlight; three to four hours of bright sunlight being usually sufficient to completely decolourise a 15 per cent solution contained in a closed test-tube of 3 c.m. diameter. The reaction occurs still more quickly in carbon tetrachloride, but more slowly in carbon disulphide, probably because, in the latter case, the actinium rays are hindered by the intense red colour which the solution soon assumes. The weight of the decomposition product formed by the action of light on a benzene solution of triphenylmethyl amounts to about 105 per cent of the triphenylmethyl originally taken. About 65 per cent of the product is triphenylmethane, while the rest consists of products insoluble in ether (about 25 per cent) and a strongly aromatic smelling oil. The part insoluble in ether consists of at least two different substances—one unsaturated and melting at 237° , and the other saturated and melting at 194° . In carbon tetrachloride no triphenylmethane is formed, but about 50 per cent of an oil result besides a crystalline mixture not yet investigated. No hexaphenyl ethane is formed in either case. These facts seem to show that the benzene plays some part in the transposition, possibly that of a reducing agent. It is noteworthy that while Kahlbaum's triphenylmethane, when its solution in benzene is exposed to direct light, gave small quantities of an insoluble substance melting at 256° , a very carefully purified specimen of the same hydrocarbon, even after exposure to direct sunlight for two months, gave no traces whatever of this product.

New Method of converting Organic Acids into Esters.—A. Werner and W. Seybold.—By the action of dimethyl sulphate on aqueous solutions of the alkali salts of organic acids the methyl esters of the acids can be obtained. The yield is often exceptionally good. This method can be used to prepare those esters which cannot

be prepared by the ordinary esterification methods with alcohols, e.g., 2—4—6 tribrom benzoic acid ester. A small excess of normal caustic potash is added to 5 grms. of the carboxylic acid, and then shaken for some time with the amount of dimethyl sulphate calculated to two molecules. The temperature of the mixture rises to 30° or 40°, and the ester separates out. The reaction is completed in half an hour, and then the mixture is heated for half an hour on the water-bath, to decompose the excess of dimethyl sulphate. On cooling, the free acid is removed by excess of alkali, and the ester if solid is filtered off, washed, and dried, and if it is liquid the alkaline liquid is distilled in a current of steam, when the ester passes over.

Compounds of Unsaturated Ketones with Metallic Chlorides.—Arthur Rosenheim and Walter Levy.—In compounds of inorganic haloids with organic oxygenated substances mostly very simple stoichiometric relations occur. Thus pentavalent elements—e.g., antimony—form compounds of formula MeCl_5X ; quadrivalent, MeCl_4X ; trivalent, MeCl_3X . The power of forming such compounds belongs to almost all classes of oxygenated compounds. In investigating the influence of double bonds on the composition of the addition products of substances containing oxygen the authors have succeeded in confirming Bayer and Villiger's hypothesis, that the formation of coloured hydrochloric acid compounds of dibenzalacetone is to be ascribed to the carbonyl oxygen. The first experiments showed that one double bond in the molecule of organic compound alters the intensity of the reaction when addition compounds are formed. Thus cinnamic acid, aldehyde, and ester react much more energetically than saturated compounds. The composition of the molecular compounds in the two cases is quite analogous, but their stability is much greater in the case of unsaturated than saturated compounds. With more than one double bond the reaction proceeds much more slowly, the products are intensely coloured, and the composition does not generally correspond to the above formulae. All observations confirm Straus's results, i.e., that the added molecule in unsaturated ketones does not attach itself at the double carbon bonds, and thus is independent of the number of these double bonds: for all ketones with two, three, or four double bonds form addition products of perfectly analogous composition with the same number of metallic salt or acid molecules. The authors' experiments go to show that the tendency to form addition compounds in unsaturated as in saturated compounds is due to the oxygen they contain, and that this activity on the part of the oxygen is greatly increased by the presence of double bonds in the molecule.

The so-called Magnesium Peroxide.—Otto Ruff and Emil Geisel.—The preparation of magnesium peroxide from sodium peroxide and magnesium hydrate or basic magnesium carbonate gives a very impure product. The authors have now found that by using magnesium sulphate and 30 per cent hydrogen peroxide, to which caustic soda had been added (all liquids being cooled to 0°), they obtain a peroxide which, on analysis without being dried, shows a composition of 1 molecule of magnesium oxide to 0.67 atom peroxide oxygen. On drying the preparation gives up oxygen. At from 25° to 37° and ordinary pressure, after twenty-two days the proportion is 1 molecule MgO to 0.39 peroxide oxygen, and this remains practically constant. The composition of the preparation then corresponds to the formula $\text{MgO}_2 \cdot 3\text{MgO} \cdot \text{aq}$. In presence of the water liberation of oxygen proceeds more quickly.

Electrolytic Reduction of Aromatic Esters.—Carl Mettler.—Aromatic esters, when subjected to electrolysis under suitable conditions, take up hydrogen and pass into compounds which no longer possess the most characteristic property of esters, i.e., power of being saponified by alkalis. Thus, benzoic acid methyl ester exposed to the reducing action of a lead cathode in alcoholic sulphuric acid solution, on application of sufficient current is converted into a non-saponifiable compound of boiling point 165° to 195°. By repeated fractional distillation, or by the help of certain

reagents, this can be separated into two fractions, one boiling at 201° and exhibiting all the properties of benzoyl alcohol, with which compound it is identical, while the other boils at 168°, and is pure benzyl methyl ether. Similarly for benzoic acid ethyl ether. No doubt benzaldehyde alcoholate of formula $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{OR}$ is formed as an intermediate product, but it has not yet been isolated. The halogen benzoic acids are converted chiefly into halogen alkyl ether, some alcohol being also formed. By means of suitable oxidising agents these compounds can readily be oxidised to the corresponding halogen benzaldehydes, many of which are closely related to technically important dyes.

MEETINGS FOR THE WEEK.

WEDNESDAY, 23rd.—Society of Arts, 8. "The Systematic Promotion of British Trade," by Gen. H. Morgan.

HACKNEY INSTITUTE, DALSTON LANE, N.E.

The Governing Body require the services of an ASSISTANT LECTURER in the CHEMISTRY DEPARTMENT on two evenings per week. Fee, 15s. per evening (1 two and a-half hours). Application, with testimonials, to be sent to the SECRETARY, not later than NOVEMBER 30th, 1904.

CENTRAL TECHNICAL SCHOOLS FOR CORNWALL, TRURO.

The Committee requires an ANALYTICAL CHEMIST with a sound knowledge of Agriculture. Capable of teaching; and also to assist the Principal, Professor CLARK. The Appointment is for one year, but may become permanent. Salary £200. Further particulars may be obtained from the Secretary.—Applications, with testimonials, should be sent not later than NOVEMBER 29th.

Princes Street, Truro,
November 15, 1904.

A. BLENKINSOP, Secretary.



Glew's Scintilloscope.

Brilliant Scintillations from PITCHBLÉNDE, Ra, Po, U, Th, or any source of Alpha-Rays.

A Welsbach mantle excites the extremely sensitive transparent screen of the Scintilloscope.

Scintilloscope complete, with 2 in. x 3 in. screen, charged with platinum and pitchblende respectively, in pocket case 7/6 post free.

Pieces of Pitchblende, ground flat, with sensitive screen attached, showing scintillations with any strong pocket magnifier, from 7/6 each, post free.

Radium, &c., for Lectures on fire

F. H. GLEW, 156, Clapham Road, London, S.W.

METHYLIC ALCOHOL

(Wood Spirit, Wood Naphtha)

MANUFACTURED BY

Stora Kopparbergs Bergslags Aktiebolag,
FALUN (Sweden).

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC,

As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, SHOT, &c.

SECOND EDITION.*With Illustrations.*

Price 2s. net (post free 2s. 1½d.)

Mme. CURIE'S Thesis
ON
RADIO-ACTIVE SUBSTANCES.REPRINTED from the **CHEMICAL NEWS.****CONTENTS.**

Introduction.—Historical.—Chap. I. Radio-activity of Uranium and Thorium; Radio-active Minerals.—Chap. II. Method of Research.—Chap. III. Radiation of the New Radio-active Substances.—Chap. IV. Communication of Radio-activity to Substances Initially Inactive.—Nature and Cause of the Phenomena of Radio-activity.

16, NEWCASTLE ST., FARRINGTON ST., E.C.

MELTING & BOILING-POINT TABLES.BY
THOMAS CARNELLEY,D.Sc. (Lond.), B.Sc. (Vict.), F.C.S.,
Professor of Chemistry in University College, Dundee.
The Standard and only work upon the subject.

2 Vols. Ry. 4to. 799 pp. 42s.

HARRISON & SONS, Pall Mall, London, S.W.**E. GEORGE & SONS,**
BOOKSELLERS.

161, WHITECHAPEL ROAD, LONDON, E.,

Are OPEN to PURCHASE Complete Sets
or short runs of the following:—*Chemical News, The Analyst Journal of the Chemical Society, 1848 to 1890, Journal of the Society of Chemical Industry, or the Publications of any other English or Foreign Learned and Scientific Societies.*—Libraries Purchased.
Current Catalogue of General Literature sent on application.

BRYAN CORCORAN Lim.**MILLSTONE BUILDERS,**
WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.Sole Makers of **MILBURN'S**
Patent Coroidal Stone Grinding Mills.
Especially suitable for certain materials, Wet or Dry.Works and Warehouses: **Back Church Lane.**
Parcel Dept.: **Basement of the Corn Exchange**
31, MARK LANE, LONDON.**M I C A.**Telephone
No. 2248
Avenue.**F. WIGGINS & SONS,** 10, Tower Hill, E., & London
102 & 103, Minories, E.C.,
MICA MERCHANTS.Manufacturers of Mica Goods or Electrical and ALL purposes.
Contractors to His Majesty's Government.**SILICATES OF SODA AND POTASH.**IN THE STATE OF SOLUBLE GLASS or IN CONCENTRATED SOLUTION.
FULL STRENGTH GUARANTEED.**OLDEST AND MOST RELIABLE MAKE.**

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.LONDON AGENTS—**CLIFFORD CHRISTOPHERSON & CO.,**
21, Mincing Lane, London, E.C., who hold stock ready for delivery.**BIRKBECK COLLEGE,**

Breams Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

CHEMISTRY J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS A. GRIFFITHS, D.Sc.
MATHEMATICS E. H. SMART, M.A.
BOTANY A. B. RENDLE, M.A., D.Sc.
ZOOLOGY H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY G. F. HARRIS, F.G.S.
METALLURGY, MINING,
and ASSAYING .. G. PATCHIN, A.R.S.M.
Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board,
Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories

Chemische Fabrik Eidelstedt,

ACETONE,
Chemically and Tech. pure.**METHYL-SPIRIT.****WOOD**
NAPHTHA.**METHYLENE, Type Regie.****ACETON OIL.**

&c.

Joh. Oswaldowski, Altona E.

THE CHEMICAL NEWSAND
JOURNAL OF PHYSICAL SCIENCE.Edited by **SIR WILLIAM CROOKES, F.R.S.**Published every Friday. Price 4d Annual Subscription, post
free including Indices, £1.**CHARGES FOR ADVERTISEMENTS.**

Five lines in column (about 10 words to line)	£ s. d.
Each additional line	0 3 6
Whole column	0 0 6
Whole page	1 15 0
Whole page	3 0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.**COVERS FOR BINDING.**Cloth, Gilt-lettered Covers for Binding the Half-yearly
Volumes of the**CHEMICAL NEWS**

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered
at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

THE CHEMICAL NEWS.

VOL. XC., No. 2348.

EMANIUM.

By F. GIESEL.

I HAVE already shown that a Sidot's blende screen is specially suitable for the detection of α -rays (*Berichte*, 1902, xxxv., 3610). By means of such a screen I have discovered a peculiar emanation which is emitted by a substance allied to lanthanum. This emanation characterises my substance; it was further described and its behaviour in the electric field, when the emanation passes over into a radiation, was also established.

From the beginning of my investigations I have repeatedly alluded to the possibility of my substance being identical with Debiere's thorium-actinium, which has as yet not been thoroughly investigated (*Berichte*, 1902, xxxv., 3611; 1903, xxxvi., 344; 1904, xxxvii., 1698; and *CHEMICAL NEWS*, 1904, lxxxix., 267). But as nothing was known of such an emanation of actinium, nor did any notices of it appear during the two years over which the publication of my articles extended, I have finally given the name "Emanium" to my substance, because I was led to assume that its specific properties, which I described, and which could easily be demonstrated, did not belong to actinium. Unfortunately I had no actinium at my disposal for a direct comparison. But in order that there should be no doubt on this point, when I was in Paris recently I asked M. Debiere to compare the two preparations, using a Sidot's blende screen which I had taken with me. It was then seen that the two preparations behaved exactly similarly. Meanwhile Debiere had already spoken of emanium and actinium as identical, without basing his opinion in the least upon the direct comparison suggested by me. Although I share Debiere's opinion in general, and had prepared a manuscript embodying a similar explanation, there are still two facts to which I must allude which might point to a difference between the two substances.

Professors Elster and Geitel have recently kindly determined the constants of decay of the induced activity caused by emanium. As the mean of five experiments which agreed very well together, the following decay curve has been obtained; it follows a simple exponential law:—

Time (minutes)	15	30	45	60	75	90	105	120
Volts	106.0	78.0	58.1	42.9	31.2	22.9	17.2	13.0

Thus the activity of the emanium induction falls to half its value in every 34.4 minutes. As Debiere gives forty minutes for actinium induction, a considerable difference exists. This cannot be directly explained by the somewhat different conditions under which Elster and Geitel worked, especially as they have obtained numbers agreeing perfectly with Curie's in the case of radium and thorium induction.

Secondly, the three lines which indicate the phosphorescence light of my preparations in the spectroscope have not been found in the actinium preparations.

Prof. Hartmann has succeeded in determining photographically the strongest of the three lines accurate to ± 0.1 Angström units, thus obtaining $\lambda 4885.4$. The other two lines, measured less accurately by optical methods, are $\lambda 5300$ and $\lambda 5909$ (*Phys. Zeit.*, 1904, [5], xviii., 570). As these lines could not be identified, they appear to belong to emanium, and it is yet to be discovered whether they occur in actinium also.

Thus, it is yet to be seen whether actinium and emanium are similar in every respect; till this is proved I think it advisable to retain the name emanium.

I have not ascribed any great importance to the chemical

differences between the two substances, which, in Debiere's preparation, are caused by adulteration with thorium, which is itself active, and in my preparation are caused by inactive lanthanum. But I must emphasise the fact that Debiere, for his newer preparations, used, not the thorium from pitchblende, but the cerium earths, as I did, in which he acknowledges the activity is concentrated. When in Paris I saw only these newer preparations of Debiere's, and not his thorium preparations.

I have now arranged some experiments to show how the increase or activity of emanium is to be explained. Since, in the case of emanium, the emanation (or β -radiation) is not driven off—as with radium—by heating or dissolving it, it is possible that a new solid non-volatile substance is formed. The separation of this solid substance from the emanium and rare earths must be effected by means of ammonia, since the freshly precipitated hydroxide of the rare earths loses the β -radiation.

Five to ten grms. of active preparation, which had been kept about a year, in the form of oxide obtained by igniting the oxalate, were dissolved in hydrochloric acid, the rare earths—and with them the emanium—were precipitated with ammonia and the filtrate evaporated.

After the ammonia had been driven off, a very small residue remained, which melted, and consisted principally of strontium chloride, which emitted strong β -radiation and emanation. If the strontium chloride was dissolved in water and the solution filtered until clear, the β -radiation did not disappear; it was only diminished in proportion to the dilution with water. The solution is luminescent. This is the first case to my knowledge in which a solution emits β -radiation strongly and continuously.† If the strontium is precipitated from the solution as carbonate all the activity collects in the precipitate, while the evaporated filtrate is inactive. Yet the strontium salt is not the only active substance. On applying electrolysis an almost invisible yellowish deposit is obtained on the platinum cathode; this emitted intense α - and β -radiation, but no emanation. The platinum anode also, on which nothing is externally visible, was so active that it had a decided effect on the luminescence screen, which, however, was much less than that produced by the cathode. It was noteworthy that the activity of both electrodes had vanished altogether by the next day. As the cathode precipitate pointed to the presence of a heavy metal the same solution of strontium chloride was treated with sulphuretted hydrogen. Only so slight a turbidity resulted that no trace of a precipitate was to be seen on a miniature filter. Nevertheless, its activity was very great. In contrast to the cathode precipitate the activity of the filter was hardly changed after it had been kept for weeks. The remaining strontium chloride solution also possesses considerable activity.

It is noteworthy that the strontium chloride behaves differently from the barium salt artificially rendered strongly active by emanium.‡ The latter loses its β -radiation in solution.

Thus we see that accidental or intentional adulterations of the emanium assume different kinds of active properties. These substances have been partly described already in my earlier article.

In order to make the experiments indisputable if possible, 0.1 gm. of the two purest preparations were subjected to the above treatment with ammonia. The one preparation gave an almost inactive separation, while the second gave strong β -radiation and emanation. In both cases the

† The absence of emanium in the filtrate can be shown physically by the gradual decay of the activity of the residue, which thus differs from emanium.

‡ Water saturated with radium emanation gives some β -radiation. But on heating the solution the emanation is driven off.

§ *Berichte*, 1904, xxxvii., 1698. This quotation may be supplemented by the following note.—The platinum double cyanide of the barium rendered artificially active by emanium reaches its maximum of dark colouration (dichroism) in a few days, while barium containing radium requires weeks or months, which behaviour corresponds exactly to the relative activities as there stated.

residue was so very small that a chemical examination was out of the question. The quantities of substance available were much too small; hence the experiments must be repeated with the 5 or 10 grms. first used, after the maximum radiation has again been reached.

A note may be added on the behaviour of the radium emanation (*Berichte*, 1902, xxxv., 3608).

From about 0.25 grm. of barium bromide containing radium bromide the gas occluded by the crystals and the emanation were driven off by heating in an atmosphere of carbon dioxide, collected over water and washed with carbonic acid. After absorption of the carbonic acid by caustic potash a naturally strongly active gas remained. The volume of the gas increased to at least double its original volume in two weeks. Then no further increase occurred, although it still possessed considerable activity. As I have convinced myself that this increase of volume cannot be caused by diffusion through the column of water I explain this phenomenon to myself provisionally as a decomposition of water caused by the emanation.—*Berichte*, 1904, xxxvii., 3963.

AN ATTEMPT TO EXPLAIN THE IRREGULARITIES OF THE ATOMIC WEIGHTS OF BERYLLIUM, ARGON, AND TELLURIUM.

By E. W. WETHERELL, A.R.C.S.

In the following paper I propose to point out certain relationships between the values assigned to the atomic weights of the elements, and to deduce therefrom a possible explanation of some of the marked irregularities and anomalies.

TABLE I.

Helium 4		Carbon . 12	Oxygen . 16
Neon . . 20	Magnesium 24	Silicon . 28	Sulphur . 32
	Calcium 40	Titanium 48	Chromium 52
—		Germanium 72	
—	Strontium 88		Molybdenum 96
—	Cadmium 112		
Xenon . 128		Cerium . 140	—
—	—	—	—
—	—	—	Tungsten 184
—	Mercury 200		—
—	—	Thorium 232	
—	—	—	—

If we take the number 4 and its multiples up to 4⁴, and arrange those elements of groups 0, 2, 4, and 6, which have multiples of 4 for their atomic weights, in their proper positions, according to the table of Periodic Law, we have Table I.

If in this table we insert the missing multiples of 4 we find that two multiples of 4 occasionally occur in the same space, and, moreover (with the single exception of Be), that the experimental value of these elements always lies within the limits of the two multiples which happen to occur together, e.g., Zn 65.4 lies within the limits of 64 and 68, and Sn 119 lies within the limits of 116 and 120. Ba, again, lies within the limits of 136 and 140 (the two multiples of 4 which happen to be present in the space occupied by barium). This gives us Table II.

If from Table II, we take the first three lines (Table III.) we find that all the elements of the He, Be, C, and O groups are multiples of 4, with the solitary exception of Be. Then since eleven elements agree with the rule of progressive increments of 4 and only one is exceptional, it is important to try to find some reason for the irregularity.

Be is an element which has always given trouble; its sp. heat is abnormal, it is not by any means typical of the group in which it occurs; moreover, it was doubtful for a long time whether its normal oxide was BeO or Be₂O₃, and it has many properties which are more like those of Al than those of Mg. Since the properties of an element are functions of its atomic weight, it is clear that the various unusual properties of Be are dependent on its abnormal atomic weight; in other words, we might expect by inverse reasoning that the atomic weight of Be would be abnormal since its properties are so irregular.

To attempt to elucidate the matter I propose to take an astronomical simile. If observers on another possibly habitable planet had so studied the motions of members of the solar system that they were aware that the attraction of the sun was modified by the attraction of the planets by one another, and yet possessed no telescope by which our moon could be distinguished, they would give too great a mass to the earth itself, as they would be reasoning on the mass of the earth together with that of the moon.

May it not be possible? I proffer the suggestion with all humility, that the atoms of an element may in some cases have a satellite—a minute body inseparable from the atom by any means at our disposal, yet one which may materially affect the properties of an element. Such satellite would in no way upset the law of Avogadro that equal volumes of a gas under equal pressure and temperature contain equal numbers of molecules, as the satellite is an integral part of the molecule; it might even account for the very slight deviation from the law which has been observed.

If this theory be tenable, and if we ever find means of separating the "satellite" from the "planet," we might find that the separated "planet" Be without its moon had an atomic weight of 8, and that its properties were analogous to those of Mg or Ca, whereas at present we are dealing with Be together with its moon, and the increase due to the moon has shifted Be towards aluminium.

To refer again to Table III., there is arithmetical progression from 4 to 52 if argon be taken as 36; we know, however, that argon is not only not 36 but it is so much greater than that value that it is actually higher than K. If, however, the rule holds good that every element in groups 0, 2, 4, and 6 must have a value which is a multiple of 4, or that it lies within the limits of the two multiples of 4 which happen to fall in the particular space allotted to the element; then argon (the planet) should have an atomic weight of 36, and it must then have a moon of the value of 4, which would increase the argon system to 40, thus taking it above the moonless K and up to the normal weight of the next element, calcium.

The inversion of Te and I would be accounted for in the same manner, and the "planet" Te should have an atomic weight of 124 and a satellite of 4, which would bring the

TABLE II.

Group 0 and 8.	Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.
Helium 4		Beryllium 8*		Carbon 12		Oxygen 16	
Neon 20		Magnesium 24		Silicon 28		Sulphur 32	
Argon 36 40		Calcium 40	Scandium 44	Titanium 48		Chromium 52	
A triplet 56—60 —		Zinc 64 65		Germanium 72		Selenium 76 80	
Krypton 80 84		Strontium 84 88		Zirconium 88 92		Molybdenum 96	—
A triplet 100 104	Silver 104 108	Cadmium 112		Tin 116 120	Antimony 120	Tellurium 124 128	
Xenon 128	Cæsium 132 136	Barium 136 140		Cerium 140	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—		Tungsten 184	—
A triplet 188 192	Gold 192 196	Mercury 196 200	Thallium 200 204	Lead 204 208	Bismuth 208	—	—
—	—	Radium 224 228	—	Thorium 232	—	Uranium 236 240	—
—	—	—	—	—	—	—	—

TABLE IV.

Argon 36	Potassium 39	Calcium 40
Moon 4		
Total 40	39	40
Selenium 76	Bromine 79	Krypton 80
Moon 3	Moon 1	Moon 2
Total 79	80	82
Tellurium 124	Iodine 127	Xenon 128
Moon 4		
Total 128	127	128

TABLE III.

4	8*		12	16
20	14		28	32
36 40	40	44	48	52

telluric "system" above that of iodine and up to that of the moonless xenon.

An analogous case to a somewhat lesser extent occurs in the case of Se; this element appears to be too high, and by the multiple of 4 rule its atomic weight should be 76.

If we compare the three sets of values above mentioned we have the results given in Table IV.

When the satellite is very large in comparison with the mass of the planet, as in the case of Be, the properties of the planet are altered (the satellite of Be has a mass equal to one-ninth of the mass of the beryllian system). In the same way argon may also be thrown out, since the satellite of argon is one-tenth of the mass of the argonian system, but in this case we have no proof as argon has no chemical properties. In the other case, the moon of Te is fairly small in comparison, and, consequently, Te is not thrown far out of being a typical member of its group.

Laboratory of the Agricultural Department,
Government of Mysore, India.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING OCTOBER 31ST, 1904.

By SIR WILLIAM CROOKES, F.R.S.,

and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, November 10th, 1904.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 211 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 211 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford continues low, the actual amount of rain recorded during the month is only 0.82 inch, the average for October is 2.76 inches; thus we have a deficit of 1.94 inches, which, if subtracted from the previous excess of 0.33 inch, leaves a deficit for the year of 1.61 inches, or 77 per cent on the thirty-five years' average.

Our bacteriological examinations of 382 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 386 others from special wells, standpipes, &c., making 768 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	217
New River, filtered (mean of 73 samples) ..	8
Thames, unfiltered (mean of 26 samples) ..	2449
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 203 samples) ..	11
Ditto ditto highest	173
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	271
River Lea, from the East London District clear- water wells (mean of 26 samples) ..	14

Of the 304 daily samples taken from the general filter wells of the Metropolitan Water Board, nineteen samples, or 6.2 per cent, were sterile. Only four samples, or 1.3 per cent, contained more than 100 microbes, and of these only one sample contained more than 150 microbes per c.c. The four excess samples contained an average of 130 microbes per c.c. In September eight excess samples contained an average of 159 microbes per c.c.

The various analyses conducted during the past month show that the general character of the Metropolitan supply was, both from the chemical and bacteriological point of view, remarkably good for the season of the year.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

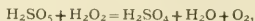
PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

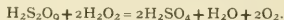
THE following completes the abstracts of papers received during the vacation and published or passed for publication in the *Transactions*:—

164. "The Effect of Colloidal Platinum on Mixtures of Caro's Persulphuric Acid with Hydrogen Peroxide." By THOMAS SLATER PRICE and JOHN ALBERT NEWTON FRIEND.

Although solutions of hydrogen peroxide and Caro's acid have no appreciable action on each other, the addition of colloidal platinum causes interaction, oxygen being evolved, according to the equation—



or—



The rate of evolution of oxygen gives a measure of the velocity of the reaction; titration methods cannot be used, since there are no accurate methods of estimating hydrogen peroxide and Caro's acid in the presence of each other. It was found that, as long as the platinum was not precipitated out of the solution, the velocity constants, whether of the second or the third order (corresponding with the above equations), continually increased. This increase is considered to be due to two causes:—(1) The gradual increase in the reactivity of the platinum during the reaction; (2) the independent and concurrent decomposition of the hydrogen peroxide and Caro's acid respectively. In some cases, the velocity curve was a straight line.

The effect of varying the concentration of the platinum was also studied, but no definite connection between concentration and velocity could be traced, except that a diminution in velocity was associated with a decrease in concentration of the platinum. In alkaline solutions, the results obtained were indefinite, since interaction takes place in the absence of platinum, and the velocity seems to depend on the rate of stirring.

165. "The Acylation of Amides." By ARTHUR WALSH TITHERLEY.

The conversion of a primary into a secondary amide and a secondary into a tertiary amide cannot, in general, be effected by treatment with acyl chlorides and anhydrides, but by first replacing the hydrogen of the —CO·NH_2 or —CO·NH·CO— group by sodium; the resulting sodium acylamide reacts usually with considerable energy with acyl chlorides, or, preferably, anhydrides, yielding acylated derivatives. Sodium benzamide and benzoic anhydride, for example, yield sodium dibenzamide and benzoate. At the same time, a tertiary amide (tribenzamide) is formed owing to the interaction of a portion of the sodium dibenzamide and benzoic anhydride.

Although the action is normal in the aromatic and aliphatic series respectively, abnormal results are obtained on attempting to apply the method to the synthesis of mixed aliphatic aromatic secondary amides. Thus, neither sodium acetamide and benzoic anhydride nor sodium benzamide and acetic anhydride yield the expected acetylbenzamide in appreciable quantity, the main product of either of these condensations being sodium dibenzamide.

Cyclic anhydrides appear to behave normally. Thus, succinic anhydride and sodium benzamide give rise to benzoylsuccinimide (needles, m. p. 180°) and s-dibenzoylsuccinimide (m. p. 211°).

A further application of sodium acylamides for the purpose of acylation is based on their condensation with esters (*Trans.*, 1902, lxxxi., 1520), but the condensation is abnormal with esters and sodium acylamides which contain the groups $\text{—CH}_2\text{·CO}_2\text{Et}$ and $\text{—CH}_2\text{·CO·NHNa}$ respectively. Methyl oxalate yields the disodium derivative of dibenzoyloxamide, but benzoyloxalimide, which was also anticipated, is not produced.

s-Dibenzoyloxamide (m. p. 227°) is readily soluble in sodium hydroxide, but the solution readily undergoes hydrolysis, forming benzamide and sodium oxalate. Ethyl succinate and sodium benzamide readily react, but do not yield either ethyl benzoyl succinamate, dibenzoylsuccinamide, or benzoylsuccinimide; the chief products are sodium succinimide and ethyl benzoate.

A very convenient process for acylating amides direct consists in treating directly with the acyl chloride the amide dissolved in pyridine (compare Freundler, *Comptes Rendus*, 1902, cxxxvi., 1553; 1903, cxxxvii., 712–714). The method is limited in the same sense as the sodium acylamide anhydride method, since in this case also aromatic acyl radicals tend to displace aliphatic groups; hence it is impossible to prepare acetylbenzamide from benzoyl chloride and a pyridine solution of acetamide. That the method may be applied to the acylation of secondary as well as primary amides is shown by the fact that dibenzamide when subjected to this process yields 50 per cent of tribenzamide.

Benzoylsuccinimide (m. p. $129\text{—}130^\circ$) is readily obtained by the action of benzoyl chloride on a pyridine solution of succinimide.

166. "The Composition of Beryl." By JAMES HOLMS POLLOCK.

The irregular results obtained on the analysis of compounds of glucina, prepared from various samples of the oxide, suggested that there was something in the composition of the beryl that had so far been overlooked.

The glucina employed was extracted from Limoges beryl during a previous research, and was known to give too high an equivalent, although analysis failed to indicate the presence of aluminium or any other base. This glucina was fractionated by crystallisation of the sulphate, by solution in ammonium carbonate, and by precipitation from hydrofluoric acid solution by potassium hydrogen fluoride. The glucina was recovered from the various fractions, converted into anhydrous chloride, and the various specimens of this salt analysed. In certain fractions, a progressive rise in the equivalent of the base was observed, giving figures ranging from 4.77 to 8.17.

Samples of glucinum chloride were then fractionated by distillation, the most volatile and least volatile portions being analysed separately. Three samples of the most volatile portions yielded equivalents of 9.08, 10.81, and 11.29.

Other fractions obtained by collecting the chloride that was first formed, apart from that which distilled over later, gave, on analysis, equivalents of 12.30, 14.80, and 15.74.

Only a small quantity of the chloride with the highest equivalent was obtained; the most careful analysis failed to detect it in the presence of aluminium, iron, or any other element, the sample having the chemical properties of glucinum only.

A spectroscopic examination of the various specimens with high equivalents showed that certain lines, only faintly visible in ordinary samples of glucina, became steadily stronger as the equivalent increased, and the known lines of glucinum became somewhat fainter.

These results indicate that beryl contains a new element having in the main the chemical properties of glucinum, but a much higher equivalent; its chloride is more volatile and more readily formed than that of glucinum, and the oxide is not so readily precipitated from a hydrofluoric acid solution by potassium hydrogen fluoride.

Ordinary Meeting, Thursday, November 3rd, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

Messrs. C. R. Beck, J. H. Johnston, R. Lessing, J. Marsh, and H. S. Shelton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Walter Henry Bentley, B.A., 18, Oaten Hill, Canterbury; John Wyclif Black, 20, Mardale Crescent, Edinburgh; Thomas Story Busher, B.A., Queen's College, Oxford; Lawrence Caldecott, 47, Woburn Place, Russell Square, W.C.; Robert John Caldwell, B.Sc., A.C.G.I., 49, Merritt Road, Crofton Park, S.E.; Peter Skinner Clark, M.B., Ch.M., Cape Town, Cape Colony, South Africa; Frederick Clarkson-Harold, 10, Fee's Terrace, Longford, Ireland; Robert Cornthwaite, Agricultural Laboratory, Halifax; William Crabb, B.Sc., The Grammar School, Penistone, Yorks; James Edward Cunningham, A.R.C.S., 21, Blenheim Gardens, Willesden Green, N.W.; Harold Deane, B.Sc., 34, Drakefield Road, Upper Tooting, S.W.; Francis Dickinson, 26, O'Connell Avenue, Berkeley Road, Dublin; Edward Evans, 33, Ranelagh Road, Westminster, S.W.; Thomas Wallace Fagan, B.A., Harper Adams Agricultural College, Newport, Salop; John Kerr Forrest, Hawsleigh, Balacava Road, St. Kilda, N.S.W.; Thomas Reginald Hodgson, The Sycamore, Poulton-le-Fylde, Lancs.; George William Thomas Horrod, 294, Brixton Hill, S.W.; John Kenneth Harold Inglis, M.A., B.Sc., University College, W.C.; Thomas Campbell James, B.A., B.Sc., 4, Belmont Terrace, Llanelli; Walter Richmond James, 49, Wednesfield Road, Wolverhampton; John Richard Johnson, Apothecaries' Hall, E.C.; Horace Francis Jones, 3, Kerry Crescent, Calne, Wilts; William App Jones, A.B., A.M., Ph.D., 12E, 18th Street, New York; Alfred Francis Joseph, A.R.C.S., 95, Marylands Road, Maida Vale, W.; James Stanley Lauder, c/o B. Harvey, Qu'Appelle, N.W.T., Assa., Canada; Arthur Garfield Levy, B.Sc., A.I.C., c/o B. Blount, Esq., 76, York Street, S.W.; James Patrick Longstaff, B.Sc., 19, Fettes Row, Edinburgh; Arthur Thomas McDougall, B.A., 3, Albion Road, College Park, S.E.; Harold Joseph Clarke Mathews, Massey's Brewery, Ltd., Burnley, Lancs.; Ernest Westby Millar, A.R.C.S., Windsor, Monkstown, Co. Dublin; Marie Jean Louis Ernest Rouillard, B.Sc., Malvern, Natal; Percy Edwin Spielmann, A.R.C.S., 21, Cadogan Gardens, S.W.; Harry Stanley, B.Sc., The Park, Southend Village, Catford,

S.E.; Thomas Sutcliffe, 19, Rhodes Street, Halifax, Yorks.; Paul John Thibault, Howell, N.S.W.; Douglas Frank Twiss, M.Sc., 89, Wood Lane, Harborne, Birmingham; Herbert Wood Watson, B.Sc., 111, Brudenell Road, Hyde Park, Leeds; William Henry Willcox, M.D., B.Sc., F.I.C., St. Mary's Hospital, W.; Frank John Wyeth, M.A., 14, Preston Drive, Brighton.

The PRESIDENT, in announcing the lamented death of Professor Lobry de Bruyn, which occurred in July, after a short illness, reminded the Society that the deceased was one of the Honorary Foreign Members elected recently. A letter of sympathy and condolence had been immediately sent in the name of the Society to the widow, and it was hoped that an obituary notice would shortly appear in the *Journal*.

Of the following papers, those marked * were read:—

*167. "Studies on the Dynamic Isomerism of α - and β -Crotonic Acids." (Part I.) By ROBERT SELBY MORRELL and EDWARD KENNETH HANSON.

To show the change in the melting-point with variation in the composition of a mixture of α - and β -crotonic acids at temperatures below the melting-point of the less fusible component (α -crotonic acid), weighed quantities of the α -acid were added to a known weight of the β -acid, and the freezing-point of the mixture observed. It was found that the freezing-point of the β -crotonic acid fell from 14.96° to a minimum of -1.1° , and then rose to 43.9° on gradual addition of the α -acid until the mixture contained 30.8 per cent of the β -acid. To complete the melting-point curve, the lowering of the freezing-point of α -crotonic acid by the β -isomerism was observed, and it was found that the curve was a continuous one from 15° through -3° (eutectic-point) to 71.9° . There is no compound of α - and β -crotonic acids between these temperatures.

The investigation on the composition of the two acids at temperatures between 100° and 168° showed that β -crotonic acid changed on heating into the α -modification, and the composition of the mixture was found by cooling the fused mass rapidly and determining its freezing-point. From the observed values of the freezing-points for known mixtures of the two acids, the composition of the mixture was fixed without having recourse to estimation by chemical methods. At 168° , the curve showing the transformation of the β -acid into the α -acid met the similar curve for the α -acid changing into the β -acid; the composition at this point was 76 and 24 per cent of the α - and β -acids respectively. The boiling-point under the ordinary pressure of a mixture of α - and β -crotonic acids is 168 – 174° (compare Michael, *Journ. Prakt. Chem.*, 1892, [2], xlv., 146).

These preliminary experiments furnish no evidence as to the existence of a compound of α - and β -crotonic acids between 100° and 168° .

*168. "The Constitution of Nitrogen Iodide." By OSWALD SILBERRAD.

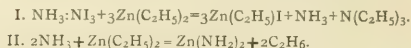
The empirical formula of nitrogen iodide has been established by Chattaway (*Am. Chem. Journ.*, 1900, xxiii., 363, 369; and 1901, xxiv., 138, 159, 318, 330, 342) as N_2I_3 , but the analytical results obtained by earlier workers showed great variations, chiefly due to unsuitable methods of preparation, insufficient precautions against the decomposing action of light, and faulty methods of analysis. In view of the methods of preparation and properties of the compound, the formula $N_2H_3I_3$ admits of two possible constitutions, $NH_3 \cdot NI_3$ and $NH_2I \cdot NH_2I$. Chattaway's work does not differentiate between these two formulae, and the earlier investigations offer no further proof as to the constitution. On the one hand, the liberation of ammonia by the action of acids supports the former configuration, whilst the formation of di-iodomethylamine by the action of methyl iodide appears to render the latter formula probable.

Non-direct derivatives of nitrogen iodide have so far been prepared in a pure state, the metallic compounds in-

vestigated have been incorrectly formulated owing to impurities in the products, and the only organic derivatives of nitrogen iodide hitherto obtained are those prepared by Stahlschmidt (*Poggendorff's Ann.*, 1863, cxix., 421) by the action of methyl iodide. These substances are so indirectly related to nitrogen iodide that they afford no definite proof as to its constitution.

In order to obtain substitution products closely related to nitrogen iodide, the action of zinc ethyl has been studied, and in this way it has been found possible to obtain direct proofs as to the constitution of the iodide.

Zinc ethyl reacts slowly with nitrogen iodide, producing volatile paraffins together with a white amorphous compound, insoluble in ether, from which ammonia and triethylamine are obtained on treatment with dilute acid and subsequent distillation with aqueous caustic potash. From this it is evident that the constitution of nitrogen iodide is represented by the formula $NH_3 \cdot NI_3$, and that the action of zinc ethyl proceeds according to the equation:—



This formula for the iodide is also supported by many of the observations of earlier investigators.

DISCUSSION.

Dr. CHATTAWAY recalled the fact that in conjunction with Dr. Orton (*Am. Chem. Journ.*, 1901, xxiv., 342) he had shown that the formula $H_3N \cdot NI_3$ alone could explain the actions which take place when nitrogen iodide is slowly decomposed by a stream of water. In such a progressive decomposition, this molecule is broken up and the ammonia washed away, while NI_3 mixed with iodine remains in the solid residue. If the ratio $N:I$ could have been obtained, the formula would have been established beyond question, but, owing to the accumulation of iodine, a possibility of experimental error was introduced, and the ratio $1:18N:I$ was the nearest approach to this on which they felt able to rely confidently; this ratio, however, excludes all formulæ except the one they put forward. Although he regarded this formula as undoubtedly correct, nevertheless, Dr. Silberrad's evidence was not quite conclusive. He drew attention to the small yield of triethylamine, and suggested that under the experimental conditions much of the base would be found in combination with ethyl iodide as tetraethylammonium iodide. It seemed unlikely that nitrogen iodide could be properly dried in quantity by washing with alcohol and afterwards with ether, especially as the compound so very readily interacted with alcohol with the production of ethyl iodide, aldehyde, and ammonia. The triethylamine obtained under these conditions might have been formed by the interaction of ethyl iodide and the liberated ammonia.

He hoped to be able shortly to publish the results obtained by the study of the interaction of nitrogen iodide and the magnesium alkyl compounds, particularly the benzyl derivatives.

Mr. SMART, in replying on behalf of Dr. Silberrad, who was absent, stated that, although ammonia was produced in quantitative yield by the interaction of nitrogen iodide and zinc ethyl, yet the proportion of triethylamine obtained in these experiments was so small that it could not be detected until the experimental conditions had been carefully worked out, and even then large quantities of the iodide had to be treated in order that the base might be isolated and identified. The personal risk involved in treating a kilogram of nitrogen iodide under ether with zinc ethyl was very small in comparison with the danger incurred in dropping the dry iodide into an ethereal solution of zinc ethyl. He believed that a pure metallic derivative of the nitrogen iodide had actually been obtained, and that a paper on this subject would shortly be communicated to the Society.

*169. "The Available Plant Food in Soils." By HERBERT INGLE.

The results of the author's investigation of the available plant food in soils lead to the following conclusions:—

1. That extraction with a 1 per cent solution of citric acid for seven days renders a soil much less fertile, especially at first, but that chemical changes in such soil, during the growth of the plants, gradually render it again capable of supplying plant food.

2. That beans are able to extract a larger portion of the potash and phosphoric acid present in the soil than barley. This was especially so in the case where extracted soil was used.

3. That Dyer's method (*Trans.*, 1894, lxx., 115) of determining "available" plant food in soils is of considerable value in estimating their relative fertility, but that another factor must be considered, namely, the rate at which the "available" plant food is renewed, especially if the soils exist under different climatic conditions.

Whilst this is probably the same or nearly so for soils under similar climatic conditions, it may be, and probably is, very different in tropical or sub-tropical soils to what it is in those of temperate climates.

DISCUSSION.

Dr. DYER said he had seen photographs of Mr. Ingle's pot culture experiments, and these certainly seemed to confirm the view that the phosphoric acid and potash soluble in 1 per cent citric acid solution corresponded with the quantity of those constituents immediately available as plant food. But the most interesting part of Mr. Ingle's work on the subject was that showing the recuperative power of soils even after they had been artificially denuded of immediately available mineral food.

170. "The Basic Properties of Oxygen: Compounds of the Ethers with Nitric Acid." By JULIUS BEREND COHEN and JOHN GATECLIFF.

In view of recently published results on the additive compounds of the ethers, the following observations, which were made early in the year, may be of interest:—In extracting with ordinary ether the products of the nitric acid oxidation of substituted toluenes, it was frequently observed that, after dehydrating and removing the ether on the water-bath, a small quantity of yellow liquid remained which had a characteristic odour, quite unlike that of ether. If this liquid were more strongly heated, or even left for a time, it decomposed with a succession of little explosions and the evolution of nitrous fumes. The liquid is produced by the action of nitric acid on ether and behaves qualitatively like a mixture of these two substances. When added to strong sulphuric acid, nitric oxide is evolved; this result being also obtained by adding strong nitric acid to a mixture of strong sulphuric acid and ether. The liquid behaves like nitric acid to phenol, benzene, and aniline. In order to ascertain whether it had a definite composition the following experiments were made:—Definite volumes of the purified ether and dilute nitric acid (1 HNO₃ : 2 H₂O) were shaken up in a separating funnel, the lower layer was removed, and the ethereal layer dehydrated for twenty-four hours over anhydrous sodium sulphate. The excess of ether was then removed by distillation until the thermometer registered 50°, when the process was stopped, for if the temperature rises above this point decomposition occurs and brown fumes are evolved. Air was now blown into the pale yellow residue contained in a beaker until the odour of ether had almost disappeared. As in this state the liquid decomposes rapidly at the ordinary temperature and slowly even at 0°, quantities of 1 to 2 grms. were rapidly weighed and made up with water to 100 c.c. A measured volume was then titrated with standard caustic soda, using methyl-orange as indicator. The following results were obtained with purified methylated ether, ethyl ether, and propyl ether:—

Ether employed.	Percentage of nitric acid in the product.	Volumes of ether and dilute nitric acid taken.	
		HNO ₃ . C.c.	Ether. C.c.
Methylated ether ..	{ 45·2	50	: 50
	{ 44·4 (a)	50	: 50
	{ 44·4	25	: 50
Ethyl ether	{ 47·3	50	: 50
	{ 47·5	50	: 50
Propyl ether	{ 33·8	50	: 50
	{ 35·9	50	: 50

(a) The ether in this case was not distilled, but evaporated at the ordinary temperature under 20 m.m. pressure.

The calculated amounts of nitric acid corresponding with the formulæ (C₂H₅)₂O, HNO₃ and (C₃H₇)₂O, HNO₃ are 46 and 38·2 per cent respectively. The agreement in the case of ethyl ether is quite satisfactory. The compound with propyl ether is evidently less stable at the ordinary temperature, the affinity for nitric acid appearing to diminish with increasing molecular weight. Amyl ether and dilute nitric acid have no interaction at the ordinary temperature, and this is also the case with dimethylquinol, the only aromatic ether investigated.

171. "The Condensation of Formaldehyde with Acetone." (A Preliminary Note). By EMIL ALPHONSE WERNER.

When acetone is mixed with a 40 per cent solution of formaldehyde, no interaction takes place until a small amount of alkali is added; if the liquids are mixed in the undiluted form, the addition of a small amount of caustic potash causes, after a few moments, a very violent reaction, the liquid boils, and an orange-red resinous condensation product separates.

When the substances are mixed in 10 per cent aqueous solution, the reaction proceeds much more slowly, the liquid gradually assumes a dark yellow colour, showing a green fluorescence; after one hour, the condensation product commences to separate as a bright orange-yellow powder, and at the end of twenty-four hours the reaction is complete. During the change, the alkalinity of the liquid diminishes considerably. The condensation product, when thoroughly washed and dried, forms an orange-yellow amorphous satiny powder with a peculiar odour. It has the empirical formula C₄H₆O; analysis gave C = 68·97 and 69·58, H = 7·46 and 7·54 per cent, whilst the calculated percentages are C 69·56, H = 7·24. The compound is freely soluble in alcohol, acetone, or glacial acetic acid, and is precipitated unchanged by water; it dissolves sparingly in benzene, chloroform, or ether. The same substance is produced whether the acetone or the formaldehyde be used in excess.

It might have been expected that a compound having the compound C₄H₆O, that is, a polymeric of CH₂:CH:CO:CH₃ (C = 68·56, H = 8·56), would have been formed; this, however, does not appear to be the case. With bromine in glacial acetic acid solution, it behaves as a saturated compound, hydrogen bromide is evolved, and a mono-brominated derivative formed, which separates on diluting with water as a dark brown powder.

The addition of hydrochloric acid to the alkaline filtrate from the original experiment produces a yellow precipitate having the same composition as the orange-yellow condensation product.

172. "The Union of Hydrogen and Chlorine. Rate of Decay of the Activity of Gaseous Chlorine." By JOSEPH WILLIAM MELLOR.

The rate at which active chlorine returns to the ordinary condition follows the exponential law $x = x_0 e^{-at}$; where x denotes activity at time t , and a and x_0 are constants (a being 2·2 approximately). This is true when the activity is induced either by the electric discharge or by exposure to light.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, November 11th, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A PAPER on the "Investigation of the Variations of Magnetic Hysteresis with Frequency," by Prof. T. R. LYLE, was read by Prof. TROUTON.

The experiments were made on two rings of laminated annealed iron, in one of which the radial breadth of the iron was considerable relative to its mean radius. These rings were magnetised by alternating currents of different strengths and periods; both the magnetising-current wave and the magnetic-flux wave were quantitatively determined by a wave-tracer (described by the author in the *Phil. Mag.*, November, 1903), and the wave-forms so obtained subjected to harmonic analysis. The experiments were divided into series, in which the period and wave-form of the magnetising current were kept as nearly constant as possible throughout any one series, while its strength was varied. The analytic expressions for the associated current and flux waves for a few series are given in tabular form. From the analytic expressions for each pair of associated waves it was found that when the magnetising current was approximately sinusoidal the total iron loss (I) was, within certain limits of the induction, given by a formula, $I = (a + bn) B^{1.57}$; where n is the number of periods per sec., B the "effective induction," and a and b are constants. When from the total iron loss per c.c. per cycle the sum of the static hysteresis and the value that theory assigns to eddy current loss was subtracted, a considerable quantity remained, which increased both when the frequency and the flux-density increased. This quantity, called by Fleming the kinetic hysteresis, has been obtained for each experiment. An interesting case of transformation and what is called reflexion of energy is drawn attention to and discussed. If the E.M.F. impressed on the magnetising circuit on the iron ring be sinusoidal, the flux-wave produced contains third, fifth, &c., harmonics. These higher flux harmonics induce currents in the magnetising circuit which are dissipated as heat in it. Thus we have a transformation of electrical energy due to alternating currents of frequency n to energy of currents whose frequencies are $3n$, $5n$, &c., which is reflected back into the magnetising circuit. This the author believes is a hitherto unnoticed source of transformer loss.

Dr. J. A. FLEMING said the paper appeared to contain many points of interest. The result given by the author, that the total iron losses varied as the 1.57 power of the induction density, agreed with practice. There was, however, no hard and fast law for the calculation of the iron losses, but the number 1.6 was useful as a guide. In many cases the loss varied according to an exponent considerably less than 1.6. He pointed out that this exponent was practically the same for all magnetic metals, and said it would be interesting to know if the law would be true in the case of a Ewing model of a magnet. The paper clearly showed that transformer losses should be determined by measuring the watts. The experimental determination of the static hysteresis was not of practical importance; what was wanted was the real loss, which varied with the frequency. We should be able to calculate the loss at any induction and frequency from the known loss at any particular induction and frequency.

Mr. A. CAMPBELL drew attention to the work of an earlier investigator on the same subject. Max Wien, in a paper on "Magnetisation by Alternating Currents" (*Wied. Ann.*, xiii., August, 1898), gives results of an investigation on the change in flux-density and hysteresis loss due to variation in frequency of the magnetising alternating current. His chief method of measurement was based on Maxwell's method of comparing two self-inductances. One of the inductive coils so compared was the winding of the iron ring under test, the source of voltage being alternating (128 to 520 ~ per sec.), and the indicating

instrument a tuned optical telephone or vibration galvanometer. The bridge measurement (starting with direct current) gave the "effective" resistance and self-inductance of the ring winding, and from these (with the dimensions, &c.) were deduced the values of B and the hysteresis loss due to the fundamental component of the alternating flux, allowance for eddy-currents having been made. A number of conclusions are drawn from the results; amongst others, that increase of frequency decreases B for a given value of H , and increases the hysteresis loss for a given value of B . This appears to indicate that with quickly alternating fields B lags behind H . It is interesting to notice that for one of the rings tested the "kinetic hysteresis" found for $n=128$ is of somewhat the same order of magnitude as that given by the rings of Prof. Lyle at lower frequencies.

The SECRETARY read a letter from Dr. D. K. MORRIS giving particulars of similar experiments carried out at the University of Birmingham.

Mr. T. H. BLAKESLEY said that ten or twelve years ago he read a paper before the Society describing experiments which pointed to the existence of kinetic hysteresis. The present paper substantiated what he had said then.

A paper "On the Practical Determination of the Mean Spherical Candle-power of Incandescent and Arc Lamps," by Mr. G. B. DYKE, was read by the Author.

Mr. Dyke points out the need of an improved method of expressing the efficiency of glow-lamps, and adopts the suggestion of Dr. Fleming of expressing the whole flux of light in lumens per watt. The expression of the efficiency in this manner involves the determination of the mean spherical candle-power (M.S.C.P.), and the paper describes a method of doing this. The objects of the paper are (1) to obtain curves showing the variations of candle-power of glow-lamps in a horizontal plane, (2) to obtain reduction factors by which the mean horizontal candle-power (M.H.C.P.) may be calculated from the maximum horizontal candle-power (C.P.), and (3) to obtain reduction factors for deducing the M.S.C.P. from the M.H.C.P. and from the C.P.

A self-contained motor-driven lamp-holder is described which rotates the lamp about a vertical axis at from 230 to 300 revolutions per minute. The M.H.C.P. was determined by spinning the lamps, and by taking C.P.s. in different azimuths by a step-to-step method. The results agreed within the limits of experimental error, thus showing that the filaments were not sensibly distorted during rotation.

An integrating photometer was used to determine the ratio (M.S.C.P.)/(M.H.C.P.). This instrument is of the type suggested by Mr. C. P. Matthews, and consists of several pairs of mirrors placed around the circumference of a semicircle, and so arranged that light emitted from a source placed at the centre of the system is incident upon the photometer screen, also situate at the centre, at the same angle with the vertical as it made on emission from the source. It is shown how the ratio (M.S.C.P.)/(M.H.C.P.) can be determined by observing one distance after obtaining a photometric balance. The effects of any departure from Lambert's cosine law and of varying reflection coefficients of the mirrors were investigated and allowed for. It was also found impossible to reduce the size of the apparatus by interposing ground-glass screens because of the varying absorption of ground-glass for light of different colours. Nine types of glow-lamp were experimented upon, and the high peaks and depressions on the curves of horizontal intensity were ascribed respectively to a mirror action of the bulb, and to portions of the filaments obstructing the light from other portions. Values of the ratios (M.H.C.P.)/(C.P.), (M.S.C.P.)/(C.P.), and (M.S.C.P.)/(M.H.C.P.), have been obtained, and for lamps of the same type of filament it is found that the ratio (M.S.C.P.)/(M.H.C.P.) is remarkably constant. The author therefore suggests the determination of the M.H.C.P. by means of a rotator, and then, with the aid of a reduction factor, determined once and for all for a particular type of

filament by an integrating photometer, the deduction of the M.S.C.P. Preliminary experiments upon arc-lamps seem to show that a similar method may be adopted for the determination of their M.S.C.P.

Dr. J. A. FLEMING congratulated the author, and referred to the peculiar difficulties under which the research had been conducted at University College. Two features of the integrating photometer used were the possibility of compensating departures from the cosine law by the setting of the mirrors and the determination of the M.S.C.P. from one reading. It was now as easy to obtain a value for the M.S.C.P. as to obtain a useless measure of the horizontal intensity in any particular direction. The variation in the reflecting powers of the mirrors due to dust and dirt could also be eliminated.

Mr. PATTERSON gave an account of similar experiments which were being carried out at the National Physical Laboratory. Referring to the fact that the author had taken for his zero position in determining the ordinary C.P. of a lamp, that in which the mean plane of the filament was at right angles to the axis of the photometric bench, he pointed out that this position was unsatisfactory because of the prevalence of streaks and shadows on the screen. The M.H.C.P., and not the C.P. in any particular direction, was the only unit now in use. The results of the author were in close agreement with those obtained at the National Physical Laboratory.

Mr. W. DUDELL pointed out that if the peaks in the curves of horizontal intensity were due to reflection from the bulb, one would expect that their position would vary with the distance between the lamp and screen. He asked the author if he had noticed any such variation. The integrating photometer described in the paper was very cumbersome, and he would like to know in what respects it was superior to Blondel's lumenmeter.

Dr. C. CHREE remarked that it would be interesting mathematically to express the illumination in a series of spherical harmonics.

The CHAIRMAN expressed his interest in the fact that some of the results of the author had been confirmed by Mr. Patterson at the National Physical Laboratory. He had recently been in America, and found that the integrating photometer was in use for measurements upon arc-lamps, but that incandescent lamps were measured with a rotator, no particular regard being paid to the M.S.C.P. With regard to the observations of Dr. Chree, he said that Mr. Patterson could give him sufficient details to carry out the calculations.

The AUTHOR, in reply to Mr. Duddell, said that although he had not varied the distance between the lamp and the screen, he had taken photographs of the "blaze" of the lamp at different distances, and found that it was always the same.

Exhibition of Apparatus by Mr. R. W. PAUL.

The construction of highly sensitive pivoted electrical instruments has been rendered difficult by the fact that delicate pivots will not admit of transporting without injury. A number of galvanometers were shown in which the design was based upon the use of a moving coil, supported on one pivot in a powerful and uniform magnetic field, and controlled by a spring. The adoption of one, in place of the usual two pivots, renders it feasible to raise the coil when the instrument is out of use, and thus secure the pivot from risk of injury. By taking advantage of this, and the incidental reduction of pivot friction, a practical instrument has been made approaching in sensibility to that of a reflecting galvanometer. Some of the instruments exhibited gave a full scale-reading of 100 divisions for 2 millivolts or for 60 micro-amperes. Combined with shunts and resistances other forms gave direct reading insulation measurements to 2500 megohms, pressures to 500 volts, and currents to 25 milli-amperes in the one apparatus. Demonstrations were given of the suitability of the galvanometers for pyrometer use. The galvanometers are so designed that accurate levelling is unnecessary. A simple

non-reflecting, suspended-coil galvanometer for the student's use, with a sensibility of one division per micro-ampere, was also exhibited.

A new design of lantern, adapted for science lectures, and for use with a powerful arrangement of Nernst filaments arranged closely together, was shown in action. It is capable of being instantly changed from horizontal to vertical projection, can be fitted with a reversing prism, and has a wide adjustment for focussing. Another exhibit was an Ayrton Mather reflecting electrostatic voltmeter with a magnetic damping device. The instrument shown had a sensibility of 500 m.m. at 1 m. for 30 volts, but similar instruments are made to give this deflection with pressures as low as 8 volts.

NOTICES OF BOOKS

Elements of Inorganic Chemistry. ("Éléments de Chimie Inorganique"). By Prof. Dr. W. OSTWALD. Translated into French by L. LAZARD. Part I. *Metalloids*. With 106 Figures in the Text. Paris: Gauthier-Villars. 1904. Pp. 542.

THE object of this work is to bring the student at once in contact with modern conceptions instead of first teaching him old and insufficient theories which have to be eventually replaced by others. For this purpose it has been necessary to modify considerably the plan on which most text-books on chemistry are written.

The author has retained the historic order of chemical science, though it might have been an advantage to elaborate, first of all, a certain number of principles, and only to give the descriptions of chemical substances for the purpose of illustrating or clearing up these general laws.

Such a book as this appeals to two classes of readers, the teachers and the pupils; it has thus a double duty to perform, which has naturally increased the difficulties met with by the author. He has, however, always leaned towards the side of the student; that is to say, he has made his descriptions more explicit than would have been necessary had he been addressing the teachers only.

The book is divided into nineteen chapters, commencing with "General Principles." He then deals with oxygen, hydrogen, water, and peroxide of hydrogen; these subjects bring us to Chapter VIII. Chapters IX. to XI. deal with chlorine, bromine, iodine, and fluorine; while Chapter XII., a long one, is devoted to sulphur and its compounds, and Chapter XIII. to selenium and tellurium. We then have five chapters dealing respectively with nitrogen, phosphorus, carbon, silicon, and boron; while Chapter XIX., the last, is on argon, and the analogous elements, helium, neon, krypton, and xenon.

There is a good table of contents, but unfortunately no alphabetical index.

Elementary Manual for the Chemical Laboratory. By LOUIS WARNER RIGGS, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

THIS manual provides students with a guide for one year's laboratory work, assuming that they are attending a suitable lecture course at the same time. The students who use the book are supposed to have no previous knowledge of chemistry, though they are not to be altogether ignorant of physics, and the demonstrator is warned that he will probably be required to teach the students arithmetical analysis, with which subject, apparently, first year college students in America are generally unfamiliar. The experiments are chosen with a special view to the requirements of large classes of from 30 to 40 students, and are divided into three parts. The first deals with general chemistry, the lecture course following the older method which was

universally adopted in teaching chemistry in England ten years ago. Thus the first lecture is devoted to defining and explaining various chemical and physical terms, which are then illustrated in the laboratory by the examination of the properties of sulphur. Then hydrogen, oxygen, and their compounds would be taken up in lecture, and prepared and examined in the laboratory, followed by a discussion of the laws of chemical action and the atomic theory, which are illustrated by a few practical examples of the preparation of a compound from its constituent elements; these experiments, however, miss their mark, since no attempt is made to perform them quantitatively. And so on through all the elements. The extremely difficult problem of what to explain at length, such as the meaning of "weigh accurately about 2 grms.," and the method of folding filter-papers, and what to leave to a few words from the demonstrator, has not been very satisfactorily solved. The second part deals with the study of volumetric analysis, in which a good course is given, followed by a few pages on the gravimetric analysis of a single compound, magnesium sulphate, the student being directed to read general directions for gravimetric work in some other manual of quantitative analysis. In the last section, the general principles of qualitative analysis are described, using ionic notation throughout; no separation tables are given, the author being of the opinion that they are better omitted in a first year's work. Some peculiarities of nomenclature, e.g., the description of magnesium as a basylous element and the spelling will militate against the use of the book in English laboratories, and there will be found no lack of choice among considerably better books on practical chemistry.

Lectures Scientifiques. ("A French Reader for Science Students"). By W. G. HARTOG, B.A. London: Rivingtons. 1904.

This book is intended specially for the use of candidates at the examinations for the science degrees of the University of London, who are now required to show sufficient acquaintance with French and German to enable them to read scientific papers in these languages. The author has found a difficulty in providing his students with suitable and sufficient material, and has accordingly published this collection of extracts on physics, chemistry, physiology, mathematics, and botany, taken from standard text-books, such as Hoefer's "*Histoire de la Physique*." The extracts are excellently chosen, so that an intelligent student who reads through them can hardly fail to become thoroughly at home among the terms and phraseology of these sciences in French. The papers on botany, in which subject it was no doubt more difficult to obtain suitable extracts, will perhaps be found the least interesting, while those on physics are in many respects the best. The book, which contains a glossary of technical words and of such as are not to be found in an ordinary dictionary, can be highly recommended as excellent for its purpose.

A Text-book of Quantitative Chemical Analysis. By J. C. OLSEN, A.M., Ph.D. New York: D. Van Nostrand Company. 1904.

It may be confidently stated that this book will rank among the best procurable on the subject of quantitative analysis. The student who uses it has placed before him a high standard at which to aim, and if he catches some of the spirit of the book he cannot fail to become an accurate and conscientious worker. In the directions for the performance of all experiments the most minute details and precautions are given as an incentive to great carefulness, and these are prefaced by admirable discussions of all the theoretical aspects of the analyses to be performed, so that before proceeding to the practical work the student should be thoroughly acquainted with the reasons for every step

he is to take. After the gravimetric determinations of metals and acids and the analysis of some few alloys and typical minerals, a short but complete course of electrolytic work is given, which alone marks the book out as specially commendable. It is curious to notice that the student is advised to weigh out exactly certain quantities of substance, since he will most probably find that he will weigh more quickly than perform the necessary calculations—a plan which most workers would hardly be inclined to adopt. In the Analysis of Technical Products it does not appear that the best choice of subjects has been made; for instance, no descriptions are given for the methods of determining sugars, which are, generally speaking, processes requiring practice and skill, and are yet quite within the powers of the average student, while the analysis of fats and oils can necessarily only be treated very cursorily. The chapters on Volumetric Analysis and Gas Analysis are excellently written and are most complete, especially in the case of the former. We have read this book from the point of view of the needs of the student, for whom the author has specially written, and by whom it will probably be most appreciated. As a work of reference for the technical chemist the omission of the determination of the less common metals, and of various plans which may be adopted when there is a likelihood of many similar determinations having to be made, will diminish its usefulness; for instance, in a technical laboratory it is well worth while to sterilise a starch solution, for which process no directions are given, instead of preparing it afresh every time it is required.

A Scheme for the Detection of the more Common Classes of Carbon Compounds. By FRANK E. WESTON, B.Sc., F.C.S. London, New York, and Bombay: Longmans, Green, and Co. 1904.

This small book will be found very useful for many purposes, quite apart from the requirements of students preparing for the Final B.Sc. Examination of London, and the Honours Chemistry Examination of the Board of Education, for whose use it is specially intended. The student of organic chemistry will find his knowledge of his lecture work is more firmly established if he supplements it by working through the experiments described here, and investigators of problems in organic chemistry will possibly discover hints for the simplest method of identifying any organic compounds passing through their hands. The descriptions of some of the experiments require fuller details and more explanation of the reactions which occur, and the form into which the information is thrown gives the book some resemblance to the old type of rule-of-thumb qualitative analysis book. However, its use will certainly help the student to systematise his knowledge of the properties and reactions of many classes of organic compounds, and it should answer its purpose as a useful practical guide in preparing for the examinations mentioned.

Grundriss der Stereochemie. ("Outlines of Stereochemistry"). By Dr. A. HANTZSCH. Second Edition. Leipzig: Johann Ambrosius Barthel. 1904.

The first edition of this book, from which translations into French, English, and Russian were prepared, was issued in 1893, and the growth of our knowledge of stereochemistry since then has rendered advisable the publication of this second revised and enlarged edition, which, while preserving the form of the original, contains some new sections on the geometrically isomeric diazo-compounds and on stereo-isomerism in complex inorganic compounds. Recent developments in such branches as the relations between configuration and biological activity and the mutual transformations of optical antipodes are treated as fully as space allows, and in this form the book is a concise and useful introduction to larger text-books of stereochemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 17, October 24, 1904.

Extraction of Vanadium from Naturally occurring Lead Vanadate, and the Preparation of certain Alloys of this Metal.—H. Herreschmidt.—The mineral, which came from the Santa Maria Mines in Spain, was smelted with coal and carbonate of soda in a reverberatory furnace. Metallic lead was formed, and a slag consisting of vanadate, aluminate, and silicate of sodium. To render this slag soluble in water, it was re-melted and air was blown into the melted mass until the vanadium was completely peroxidised. On treatment with water, 95 per cent of the vanadium present in the mineral went into solution. After precipitating out the silica, the solution was concentrated and the vanadic acid precipitated by means of sulphuric acid. For making ferro-vanadium by the electric furnace, the vanadium was precipitated from the purified solution of sodium vanadate by iron sulphate and sodium carbonate. An alloy of nickel and vanadium was made by reducing a mixture of nickel oxide and vanadic acid, the constituents being taken in the proportion necessary to obtain an alloy containing 25 per cent of vanadium.

A New Anhydride of Dulcitol.—P. Carré.—An anhydride of dulcitol can be obtained by heating this substance with phosphoric acid for some time at a temperature of 135°. The phosphoric ethers formed are saponified by water at 140°. The phosphoric acid is precipitated by baryta, the solution filtered and evaporated to a syrupy consistency. A thick yellowish liquid is obtained, which boils at 108° under a pressure of 18 m.m. Its formula by analysis is $C_6H_{10}O_4$. Various reactions prove that dulcitol contains two secondary alcohol groups, and hence its formula may be written $C_6H_6O_2(CHOH)_2$.

A New Method of Preparing Organic Derivatives of Phosphorus.—V. Auger.—White phosphorus is dissolved at 0° in alcoholic potash. This solution contains phosphorus in a low state of oxidation. On the addition of alkyl iodides, a phosphine, RPH_2 , a sub-oxide of phosphine, $(R.P)_2O$, and soluble phosphinous derivatives are obtained. This reaction seems to be of general application, since alkyl bromides and chlorides and other halogen derivatives, such as the monochloracetate of sodium, act in a similar fashion upon alkaline solutions of phosphorus.

Remarks upon a Recent Series of Calorimetric Determinations.—P. Lemoult.—The author has calculated the heat of combustion of thirty-five organic substances by means of a formula given in previous papers. He gives a table comparing his results with those recently obtained experimentally by Fischer and Wrede.

MISCELLANEOUS

Application of Permanganates to the Determination of the Constitution of the Amines and of other Ammonised Compounds.—A. Ginzberg.—The author proposed to determine, by means of permanganate, the presence of the non-saturated groups in the azotised compounds. As the amines reduce nearly the whole of this reagent after a longer or shorter lapse of time, it is best to commence by converting the substance under examination into benzene-sulphonised derivatives; these latter are only

oxidised in the cold by $KMnO_4$ when the amine contains an ethylenic function. In certain cases (an amine insoluble in water) it is advantageous to operate in a solution of acetate of ethyl, which dissolves to the extent of 1.5 per cent in $KMnO_4$, and which is not oxidised in the cold by this reagent. Experiments have been carried out on the benzene-sulphonised derivatives of the following amines:—Methylamine, fusible at 31°; dimethylamine, fusible at 47–48°; ethylamine, fusible at 57–58°; diethylamine, fusible at 42–43°; di-isobutylamine, fusible at 55–56°; aniline, fusible at 108.5–109°; methylaniline, fusible at 77.5–78°; ethylaniline, liquid; diphenylamine, fusible at 122–123°; piperidine, fusible at 92–93°; tetrahydroquinoline, fusible at 54–55°; and allylamine, fusible at 40.5–41°.—*Berichte*, vol. xxxvi., p. 2703.

Electric Conductivity of Solutions in Bromine.—V. A. Plotnikov.—Solutions in bromine of $AlBr_3$, either pure or treated with AlI_3 , do not act as electrolytes; on the other hand, solutions of the complex salts, $AlBr_3 \cdot CS_2$ and $AlBr_3 \cdot C_2H_5Br \cdot CS_2$, discovered by the author (*Bull. Soc. Chim.*, vol. xxvi., p. 605; and vol. xxx., p. 875), do conduct an electric current. Their conductivity has been examined by the Kohlrausch-Ostwald method between non-platinised electrodes (platinum black dissolves slowly in bromine). With $AlBr_3 \cdot CS_2$ the conductivity is almost nil if the solution contains only 2 or 3 per cent of the dissolved body; it increases, however, with the concentration, but diminishes rapidly on agitation, regaining its previous value when left to stand; finally, with concentrations of about 20 per cent it takes a definite value which is no longer affected by agitation; neither does it change with time; it is of the same order of value as that of aqueous solutions of ordinary salts; for example, the specific conductivity, K , of a 35 per cent solution = 0.0062. A solution of $AlBr_3 \cdot C_2H_5Br \cdot CS_2$ behaves like the preceding salt, but its conductivity is slightly higher. $SbBr_3$ is soluble in bromine, but its solutions are not good conductors; with saturated solutions (48 per cent of $SbBr_3$), $K = 98 \cdot 10^{-6}$. Dilute solutions of PBr_3 in bromine have a conductivity of almost nil, which, however, increases with the concentration; these solutions behave like those of the complex salts of $AlBr_3$; that is to say, their conductivity diminishes on agitation when they contain less than 13 per cent of PBr_3 ; with a saturated solution (36 per cent of PBr_3), $K = 0.0534$.—*Journ. Soc. Phys. Chim. R.*, vol. xxxv., p. 794.

Action of the Halogen Derivatives of the Tri- and Penta-valent Metalloids upon Alkyl Halogen Compounds.—V. Auger.—By the reaction of Crafts and Silva the iodide of triethyl phosphine is easily obtained by acting upon white phosphorus with ethyl iodide. The author has shown that if the constituents are taken in the proportion of P_2I_4 to 3RI, the most abundant product of the reaction is a dialkyl phosphinic derivative, mono- and tri-derivatives being formed at the same time. A larger proportion of the mono-derivative is formed if less alkyl iodide is used. Attempts to prepare similar compounds from the halogen derivatives of antimony, arsenic, and bismuth were unsuccessful.—*Comptes Rendus*, cxxxix., No. 18.

The Density of Nitrogen Monoxide and the Atomic Weight of Nitrogen.—A measured volume of nitrogen monoxide was absorbed in a tube containing carbon. The tube was surrounded by a mixture of solid CO_2 and ether. The increase in weight of the tube gives the weight of gas absorbed. The mean of three experiments gives 1.97788 as the weight of a normal litre of the gas. The molecular weight of the gas, determined by applying the theorem of corresponding conditions, and comparing its density with that of carbon dioxide, was found to be 46.026. This gives 14.013 as the atomic weight of nitrogen. From this and from other experiments, which give 14.011 as the mean value of the atomic weight, it seems that the value ($N = 14.04$) given in the International Table for 1904 is rather too high.—*Comptes Rendus*, cxxxix., No. 18.

Chemical Society Research Fund.—A meeting of the Research Fund Committee will be held in December next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, December 5, 1904.

MEETINGS FOR THE WEEK.

MONDAY, 28th.—Society of Arts, 8. (Cantor Lectures). "Musical Wind Instruments," by David James Blaikley.
WEDNESDAY, 30th.—Society of Arts, 8. "The British Canals Problem," by Arthur Lee, J.P.
THURSDAY, Dec. 1st.—Chemical, 8. "The Nitrates of the Alkali Metals and Metals of the Alkaline Earths, and their Decomposition by Heat," by P. C. Ray.

HACKNEY INSTITUTE, DALSTON LANE, N.E.

The Governing Body require the services of an ASSISTANT LECTURER in the CHEMISTRY DEPARTMENT on two evenings per week. Fee, 15s. per evening of two and a-half hours.
Application, with testimonials, to be sent to the SECRETARY, not later than NOVEMBER 30th, 1904.

CENTRAL TECHNICAL SCHOOLS FOR CORNWALL, TRURO.

The Committee requires an ANALYTICAL CHEMIST with a sound knowledge of Agriculture. Capable of teaching; and also to assist the Principal, Professor CLARK. The Appointment is for one year, but may become permanent. Salary £200. Further particulars may be obtained from the Secretary.—Applications, with testimonials, should be sent not later than NOVEMBER 29th.

Princes Street, Truro,
November 15, 1904.

A. BLENKINSOP, Secretary.

Chemische Fabrik Eidelstedt,

ACETONE,
Chemically and Tech. pure.
METHYL-SPIRIT.
WOOD
NAPHTHA.
METHYLENE, Type Regie.
ACETON OIL.

&c.

Joh. Oswaldowski, Altona E.

THE CHEMICAL NEWS AND JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday Price 4d Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 10 words to line)	0	3	6
Each additional line	..	..	0 6
Whole column	..	..	1 15
Whole page	..	..	3 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

MR. EDWARD ARNOLD'S NEW BOOKS.

THE CHEMICAL SYNTHESIS OF VITAL PRODUCTS

AND THE

INTER-RELATIONS BETWEEN ORGANIC COMPOUNDS

BY

R. MELDOLA, F.R.S., V.P.C.S., F.I.C., &c.,
Professor of Chemistry in the City and Guilds of London
Technical College, Finsbury.

Super Royal 8vo. 21s. net.

THE BECQUEREL RAYS AND THE PROPERTIES OF RADIUM.

By the Hon. R. J. STRUTT,
Fellow of Trinity College, Cambridge.

Demy 8vo. With Diagrams. 8s. 6d. net.

AN INTRODUCTION TO THE THEORY OF OPTICS.

By ARTHUR SCHUSTER, Ph.D., Sc.D., F.R.S.,
Professor of Physics at the University of Manchester.

Demy 8vo. With numerous Diagrams. 15s. net.

THE ELECTRIC FURNACE.

By HENRI MOISSAN,
Professor of Chemistry at the Sorbonne.

Translated by A. T. de MOUILPIED, M.Sc., Ph.D.
Demy 8vo. With numerous Illustrations. 10s. 6d. net.

London: EDWARD ARNOLD, 41 & 43, Maddox St., W.

MELTING & BOILING-POINT TABLES.

BY

THOMAS CARNELLEY,
D.Sc. (Lond.), B.Sc. (Vict.), F.C.S.,
Professor of Chemistry in University College, Dundee.
The Standard and only work upon the subject.

2 Vols. Ry. 4to. 799 pp. 42s.

HARRISON & SONS, Pall Mall, London, S.W.

E. GEORGE & SONS, BOOKSELLERS,

151, WHITECHAPEL ROAD, LONDON, E.,

ARE OPEN TO PURCHASE Complete Sets
or short runs of the following:—*Chemical News*, *The Analyst*,
Journal of the Chemical Society, 1848 to 1890, *Journal of the Society*
of Chemical Industry, or the Publications of any other English or
Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC

As described in the "Report of the Inland Revenue Departmental
Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET
LEAD and PIPE, LITHARGE, SHOT, &c

THE CHEMICAL NEWS.

VOL. XC., No. 2349.

AN ATTEMPT TO EXPLAIN THE OCCURRENCE OF ZINC, CADMIUM, AND MERCURY IN THE SAME GROUP WITH THE ALKALINE EARTHS. AND OF TIN AND LEAD IN THE CARBON GROUP, AND OF COPPER, SILVER, AND GOLD IN THE SAME GROUP WITH THE ALKALINE METALS.

By E. W. WETHERELL, A.R.C.S.

In my previous paper (CHEMICAL NEWS, vol. xc., p. 260, November 25, 1905) on the anomalies of beryllium, argon, and tellurium, I suggested that the irregularities might be due to the presence of satellites to the atoms of those elements, and for that purpose I drew up a table which showed that every element of groups 0, 2, 4, and 6 was a direct multiple of 4, or that it lay between the limits of the two multiples of 4 which happened to lie in the same space. I now find that the elements which have almost exact multiples of 4 are more typical of their groups than those which lie between two multiples, and it has therefore appeared to me that it is possible that only one multiple can occur in any one space, and that the deviation of an element is due in other cases to the presence of a satellite. I find by calculations that the lowest multiple of 4 for zinc is 64, for cadmium 108, and for mercury 196 (*vide* table in previous article); these atomic weights would require such relatively large satellites to bring them up to their experimental value that the peculiar properties of these metals (which distinguish them from the alkaline earths) may be due to satellites. If these elements had no satellites their true atomic weights would be 64, 108, and 196 respectively, and these elements, α -zinc, α -cadmium, and α -mercury, would be alkaline earths. In this connection I may mention that the possible satellite of barium is only 1.2, which is so small relatively to the weight of α -barium, that it has little effect on the characters of barium. It seems to me not an impossibility that these satellites have some action in preventing the linking of the atoms of Zn, Cd, and Hg in the free state, for it is well known that these three metals are monatomic.

To turn to the carbon group. It is patent to the most casual observer that tin and lead stray far from the typical elements of the carbon group in many of their characters. I find, on the multiple of 4 theory, that all the other members of the carbon group can have no satellites (or very small ones), but that as tin and lead should have atomic weights of 116 and 204 respectively that they must have comparatively large ones. In this case, again, the satellite has the effect of making the elements more metallic, more easily reducible, and less ready to be acted upon by the atmospheric agents.

In the case of copper, silver, and gold their atomic weights should be 60, 104, and 192 respectively; consequently, large satellites are necessary to bring these values up to the weights determined by experiment; here again the effect of the satellites has been to render these elements less alterable.

If the table of the Periodic Law holds good, there should be analogues of copper, zinc, and tin in the interval between cerium and tantalum; it should be easy to calculate their "planet and satellite" values in the following way:—The difference between "planetary" copper and "planetary" silver is 44, and between "planetary" silver and "planetary" gold is 88; consequently, the analogue will be 44 more

than silver and 44 less than gold; this will give the value for the "planet" of 148. Such an element without a satellite would be an analogue of sodium; but it is much more probable that it will have a satellite of about the value of 4; it will then be a metal not acted upon by atmospheric oxygen, only slightly acted upon by sulphur vapours, occurring native in minute quantities (probably associated with gold and silver), crystallising in the cubic system, and having an atomic weight which experiment will show to be 150—153.

The same rule of intervals of 44 occurs between "planetary" zinc 64 and "planetary" cadmium 108, and the same interval of 88 between "planetary" cadmium and "planetary" mercury; hence the calculation for the analogue is the same. If the element has an atomic weight of 152 it will have the characters of magnesium, but if the "satellite" is present it will be close to cadmium in its properties, but probably even less alterable. It will probably be found to have an atomic weight of 156.

The interval between "planetary" tin and "planetary" lead is again 88, and the missing analogue should have an atomic weight of 160, and if no satellite is present it will resemble silicon. If a satellite of about the value of 3 is present the atomic weight will be 163, and the characters will be analogous to tin and lead.

Laboratory of the Agricultural Department,
Government of Mysore, India.

THE ABSORPTION OF HYDROGEN BY RHODIUM. By L. QUENNESSEN.

In the course of researches on metals allied to platinum, I have been led to modify certain properties mentioned by former writers.

Thus, according to Th. Wilm (2), pure rhodium should possess a capacity of absorbing hydrogen much greater than that of platinum, and this assertion is reproduced to-day in different works. Wilm further announced that this absorptive property varied with the method of preparation of the metal; for example, that the rhodium obtained by calcination of the double chlorammonium salt had a higher absorbent power than the metal obtained with the double chloride of sodium or of potassium, and that this absorption was apparently due to a chemical affinity of the metal for hydrogen.

My experiments in no wise confirm these facts.

Some rhodium, mixed with sodium chloride, fused and powdered, was treated with a current of chlorine at 440°; then, in order to remove the impurities which might remain, the product was taken up with water and converted into the double nitrite of rhodium and sodium. The latter salt was divided into two portions; one was re-converted by hydrochloric acid into the double chloride of sodium and rhodium, and the other into the double chloride of rhodium and ammonium, this being obtained perfectly pure by treating the double nitrite of sodium with ammonium chloride in order to make the double ammoniacal nitrite and the latter by hydrochloric acid.

These two compounds were then heated and reduced at a red heat in a current of pure dry hydrogen, in which the rhodium was allowed to cool.

In the case of the double salt of sodium, the precaution was also taken of removing the alkaline chloride by washing with warm water and repeating the hydrogen treatment under the same conditions.

If, after cooling is complete, the tube containing the boat with the rhodium is opened, one detects, with the entrance of air, the simultaneous formation of water vapour, which condenses on the glass, whilst, if the atmosphere of hydrogen is expelled by a current of pure dry carbon dioxide, the phenomenon of formation of water upon contact with the air is not produced.

Further, if the boat with the rhodium is placed in a vacuum and heated to 440° by means of the sulphur bottle, the barometric column attached to the apparatus indicates no variation of pressure, and it is quite impossible to extract from it the least bubble of gas by means of the mercury tube.

These experiments, repeated at different times, always gave the same result; they therefore lead to the conclusion that rhodium is not analogous to palladium as regards chemical affinity for hydrogen, and that it acts as would platinum, condensing oxygen and hydrogen to form water.

Further, it does not appear that the rhodium obtained by decomposition of the chlorammonium salt has properties much more active than that obtained by decomposition of the sodium chloride salt when the latter has been freed by washing from the alkaline chloride which envelopes it.

THE REFRACTIVE INDICES OF THE ELEMENTS.*

By CLIVE CUTHBERTSON.

IN a letter addressed to *Nature* in October, 1902, attention was drawn to the fact that the refractivities of the five inert gases of the atmosphere, He, Ne, A, Kr, and X, as determined by Ramsay and Travers, were, within narrow limits of accuracy, in the proportion of 1, 2, 8, 12, and 20; or, more simply, of $\frac{1}{4}$, $\frac{1}{2}$, 2, 3, and 5.

In a second letter it was shown that the refractivities of the halogens, Cl, Br, and I, stand also in the relation of 2, 3, and 5 to the same degree of accuracy; but it was pointed out that the figures for P, As, and S, as measured by M. Le Roux in 1861, did not show any similar relation; and it was observed that a re-determination of them would be interesting.

With a Jamin's refractometer, adapted for use with high temperatures, results have now been obtained for Hg, P, and S, which differ widely from those of M. Le Roux. The index of mercury, calculated for a molecule containing two atoms, is placed at 1.00857, a number which agrees closely with the value given by the refractive equivalent of Gladstone. The index of P₂ is found to be 1.001197 and that of S₂ is 1.001010.

In all three cases it is estimated that the margin of error does not exceed $\frac{1}{4}$ per cent. Comparing these values for P₂ and S₂ with those of N₂ and O₂, it is shown that the simple relations found in the case of the inert gases and the halogens also hold in the case of nitrogen and phosphorus, oxygen and sulphur; and that an atom of phosphorus retards light four times as much as an atom of nitrogen, an atom of sulphur four times as much as an atom of oxygen.

Efforts have also been made to measure the index of fluorine in the gaseous state, but, owing to the experimental difficulties, success has not yet been attained.

It appears then, that, out of fourteen elements whose index of refraction has been measured in the gaseous state, twelve conform to the rule that in each chemical group the refractivities of the elements are in the ratios of small integers. The other two, Hg and H, have no allied elements with which they can be compared.

It is pointed out that N, O, and Ne are each followed, in their respective families, by an element whose refractivity is four times as great, and that, consequently, there are reasons for believing that the elements composing the series N, O, F, and Ne, and P, S, Cl, and A, are in some sense homologous. Comparing the refractivities of the latter series we see that the power to retard light appears to be closely connected with the valency, increasing as it increases, in spite of the decrease in atomic weight as shown in the following table:—

	Element.			
	P.	S.	Cl.	A.
Atomic weight ..	31	32	35.5	40
Refractivity ..	299×4	275×4	192×4	141×4

The series Ne, O, N, show the same relation, and it is probable that the refractivity of C is even higher than that of N.

The refractivity of B, estimated from BCl₃ and BBr₃, is certainly very great; but whether it exceeds that of C there is not sufficient evidence to determine.

HYDRONITRIC ACID AND THE INORGANIC TRINITRIDES.*

By L. M. DENNIS and A. W. BROWNE.

THE following paper contains:—I. A brief historical review of the work published up to the present time upon hydronitric acid and the inorganic trinitrides. II. An experimental study of (A) the method of W. Wislicenus for preparing hydronitric acid, (B) the composition of certain inorganic trinitrides, (C) a method for the detection of hydronitric acid and inorganic trinitrides, and (D) the reaction between hydronitric acid and potassium permanganate in the presence of sulphuric acid.

I. HISTORICAL.

Under this head will be considered—(1) The methods of preparing hydronitric acid, (2) the inorganic compounds of hydronitric acid and the methods of preparing them, and (3) the properties and reactions of hydronitric acid and the inorganic trinitrides. The organic derivatives will be considered in the present work only in so far as they are of interest in the preparation of the acid.

At the outset it may be well to discuss the question of nomenclature. A variety of names for the acid and its derivatives have been used by English and American investigators and writers. The name *azimide* has perhaps been most frequently used to designate the acid. This has the disadvantage of neither expressing the acid character of the compound nor indicating its close analogy to the halogen hydrazides. Among other names which have been used are *hydrazotic acid* (*Journ. Chem. Soc.*, lxxvii., 705); *triazotic acid*, derivatives called respectively *azides* and *triazates* (H. C. Jones, "Principles of Inorganic Chemistry," p. 208, the Macmillan Company, New York, 1903); *hydronitrous acid* (Mendeleeff's "Principles of Chemistry," 2nd English edition by Kamensky and Lawson, vol. i., p. 265, Longmans, Green, and Co., London, 1897); *hydrogen nitride* (*Journ. Chem. Soc.*, [1], lx., 56, 524); and *nitrogen hydride* (*Journ. Chem. Soc.*, [1], lx., 394).

In the publications from the Cornell University Laboratory the term hydronitric acid has been employed for the following reasons:—

In English usage the prefix "hydro" connotes the absence of oxygen, and acids bearing this prefix have also the termination "ic." The name employed is derived from nitrogen instead of azote, for the reason that while both are of Greek origin, nitrogen is distinctly a word of English usage, while azote is still to be regarded as a foreign word that has not yet received adoption into our language. Following the analogy between the term hydronitric acid and the names of the halogen acids, such as hydrochloric acid, the salts of hydronitric acid would normally be termed nitrides, but a distinct group of nitrides—of which potassium nitride, K₃N, may be cited as an example—has long been known. Consequently, the term "trinitride" was adopted to distinguish the salts of hydronitric acid from this other group of nitrides, and the termination "ide" is employed to show that the compounds contain no oxygen. In further recognition of the analogy between

* Abstract of a Paper read before the Royal Society, November 24, 1904.

* From the *Journal of the American Chemical Society*, xxvi., No. 5.

the trinitrides and halides, it is suggested that the ring of three nitrogen atoms be called the nitrine group, and that the hypothetical compound, $(N_3)_2$, analogous to the chlorine, bromine, or iodine molecule, be called nitrine.

1. Methods for Preparing Hydronitric Acid.

The methods employed by various investigators in the preparation of hydronitric acid may be classified under five heads:—

a. Methods involving the action of a compound containing a chain of two nitrogen atoms united to positive atoms or radicals upon a compound containing a single nitrogen atom united to negative atoms or radicals.

b. Methods involving the action of a compound containing a chain of two nitrogen atoms united to negative atoms or radicals upon a compound containing a single nitrogen atom united to positive atoms or radicals.

c. Methods involving the simultaneous oxidation of two compounds, one of which contains a chain of two nitrogen atoms, the other a single nitrogen atom, and both of which are united to positive atoms.

d. Methods involving the decomposition of a compound containing a chain of three or more nitrogen atoms.

e. Methods involving the hydrolysis of aromatic derivatives of hydronitric acid.

A possible new class of methods, which has received as yet no experimental attention, is the converse of c. This class will include methods involving simultaneous reduction of two compounds, one of which contains a chain of two nitrogen atoms, the other a single nitrogen atom, and both of which are united to negative atoms.

a. The reactions involved in the methods under this head may, in their simplest form, be expressed by the typical equation $NH_2.NH_2 + NO_2H = HN_3 + 2H_2O$.

The now classical experiments which led Curtius (*Ber.*, xxiii., 3023), in 1890, to the discovery of hydronitric acid, consisted in the preparation of benzoyltrinitride by the action of nitrous acid upon benzoylhydrazine.

By saponifying the benzoyltrinitride with sodium hydroxide he obtained sodium trinitride, from which he was able to prepare free hydronitric acid by distillation with sulphuric acid.

Subsequently he used, instead of sodium hydroxide, sodium ethylate (*Ber.*, xxiv., 3341) and alcoholic ammonia (*Ber.*, xxix., 759).

In 1893 Curtius (*Ber.*, xxvi., 1263) found that a dilute aqueous solution of hydronitric acid could be obtained by leading the red gases evolved from a mixture of nitric acid and arsenic trioxide into a dilute ice-cold solution of hydrazine hydrate, or by adding the blue solution obtained by condensing the red gases upon ice. This method he considered particularly adapted for lecture-room purposes.

At about the same time, Angeli (*Attd. Reale Accad.*, [5], ii., 1, 569; *Centrbl.*, 1893, ii., 559) prepared silver trinitride by adding a solution of hydrazine sulphate to a cold saturated solution of silver nitrate.

Dennstedt and Göhlich (*Chem. Zeit.*, xxi., 876), in 1897, described the preparation of hydronitric acid by the interaction of hydrazine sulphate and potassium nitrite.

In 1899 Sabanejeff and Dengin (*Zeit. Anorg. Chem.*, xx., 21) found that by gently heating in a test-tube a mixture of 1.5 grms. of hydrazine sulphate and 4 c.c. of nitric acid (density 1.3), they could obtain hydronitric acid as one of the reaction products. The yield amounted to from 10 to 12 per cent of the hydrazine sulphate used. The method is recommended by its author as an especially available one for lecture-room work.

In the same year, Tanatar (*Ber.*, xxxii., 1399) devised a method for preparing hydronitric acid by the action of nitrogen trichloride upon hydrazine.

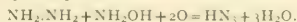
b. The reaction typical of this class of methods may be expressed by the equation $NH_3 + N_2O = NH_3 + H_2O$.

W. Wislicenus (*Ber.*, xxv., 2084) stated in 1892 that he was unable to prepare the acid by direct union of the two substances, but that its sodium salt could be obtained by

passing dry nitrous oxide over sodium amide heated to a temperature of between 150° and 250°.

A detailed experimental study of the method of Wislicenus will be found below.

c. The typical reaction for this class of methods is expressed by the equation—



In 1902 Tanatar found that when a molecular mixture of hydrazine and hydroxylamine salts was oxidised in acid solution by bromine water, permanganic acid, lead dioxide or red lead, a small quantity of hydronitric acid was invariably formed. With hydrogen peroxide a yield of 24.3 per cent, and with chromic acid a yield of 29.27 per cent was obtained (*Ber.*, xxxv., 1810).

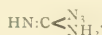
d. In 1892 Thiele (*Lieb's Ann. Chem.*, cclxx., 1) obtained hydronitric acid by decomposing the salts of diazoguandine.

Freund and Schander (*Ber.*, xxix., 2500) obtained hydronitric acid by the action of an alkali upon aminotriazasulphol,—



It will be seen that both methods thus far considered under this head may be looked upon as involving the decomposition of compounds that are derivatives of the hypothetical compound of hydrogen and nitrogen, $NH_2.H:NH$.

In the opinion of Hantzsch and Vogt (*Lieb's Ann. Chem.*, cccxiv., 339), however, the so-called diazoguandine is not to be regarded as a real diazo-compound, but as a trinitride with this structure:—



The method of Angeli, given above, might be regarded as a member of this class of methods if the possible formation of the intermediate product is considered of any importance.

In 1893 Curtius (*Ber.*, xxvi., 1263) found that, by the action of certain diazo-compounds upon hydrazine or certain of its primary substitution products, he in all probability obtained derivatives of the hypothetical compound of hydrogen and nitrogen, $NH_2.NH.N:NH$, which he called butylene.

e. Methods of obtaining hydronitric acid by the hydrolysis of aromatic trinitrides are perhaps not of the same theoretical interest as those described above, as the former start from compounds already containing the nitrine group, and prepared by some other method. Work done upon the subject has, however, brought out still further the interesting analogy between the trinitrides and the chlorides, by showing that the replaceability of the nitrine group, as well as of the chlorine atom, is increased by the introduction of certain groups into the benzene ring.

As illustrative of methods of this class, the work of Nöling and Grandmougin (*Ber.*, xxiv., 2546), and of Nöling, Grandmougin, and Michel may be cited (*Ber.*, xxv., 3328).

Later, Michel (*Moniteur Scientifique*, [4], vii., II., 749) extended the experiments of the above mentioned investigators, and confirmed the conclusion already indicated by them, that aromatic trinitrides containing negative radicals in the ortho- or para-position may be hydrolysed by the action of alcoholic potassium hydroxide, while the meta-substitution products do not so react.

In so far as any attempt has been made by different authors to compare the above methods for preparing hydronitric acid on the basis of practical utility, the almost unanimous verdict seems to be that the method of Wislicenus is on the whole the most satisfactory. One

reviewer speaks of the nitrogen trichloride method of Tanatar as the one next to be preferred (Harden, *Journ. Chem. Soc.*, lxxvi., II., 479).

2. Inorganic Compounds of Hydronitric Acid.

In 1890, Curtius (*Ber.*, xxiii., 3023) briefly described the trinitrides of silver AgN_3 , mercury Hg_2N_6 , and barium BaN_6 . He also mentioned the existence of the ferrous, cuprous, sodium, and ammonium trinitrides. In 1891 (*Ber.*, xxiv., 3341), he further described some of the same compounds, and also the trinitrides of lead and diammonium, $\text{N}_2\text{H}_5\text{N}_3$.

In 1896, Dennis and Doan (*Journ. Am. Chem. Soc.*, xviii., 970) prepared thallous trinitride, TlN_3 , and thallous-thallic trinitride, $\text{TlN}_3\cdot\text{TlN}_3$.

In 1898 Dennis and Benedict (*Journ. Am. Chem. Soc.*, xx., 225; *Zeit. Anorg. Chem.*, xvii., 18), in the course of a general investigation upon the trinitrides of the alkali and alkaline earth metals, prepared the trinitrides of lithium $\text{LiN}_3\cdot\text{H}_2\text{O}$, sodium, potassium KN_3 , rubidium RbN_3 , and caesium CsN_3 , and the trinitrides of calcium CaN_6 , strontium SrN_6 , and barium $\text{BaN}_6\cdot\text{H}_2\text{O}$.

In the same year Curtius and Rissom (*Journ. Prakt. Chem.*, [2], lviii., 261) prepared the following compounds:—Ammonium, lithium LiN_3 , sodium, potassium, rubidium, caesium, thallium, calcium, strontium, barium, diammonium, cadmium CdN_6 , pyridine cadmium $(\text{C}_5\text{H}_5\text{N})_2\text{N}_6\text{Cd}$, and cupric CuN_6 trinitrides; also basic trinitrides of zinc $\text{ZnN}_3\cdot\text{OH}$ (?), manganese $\text{MnN}_3\cdot\text{OH}$, nickel $\text{NiN}_3\cdot\text{OH}$ (?), cobalt $\text{CoN}_3\cdot\text{OH}$, and chromium (ratio $3\text{Cr} : 2\text{N}_3$); and double trinitrides of cobalt and potassium $\text{CoN}_6\cdot\text{KN}_3$, cobalt and ammonium $\text{CoN}_6\cdot\text{N}_4\text{H}_4$, and of nickel and potassium $\text{NiN}_6\cdot\text{KN}_3$ (?). He did not succeed in isolating the trinitrides of magnesium, beryllium, iron, aluminum, platinum, and gold.

In 1900, Curtius and Darapsky (*Journ. Prakt. Chem.*, [2], lxi., 408), in continuation of the work just described, made a further study of the behaviour of aluminum, iron, and chromium toward hydronitric acid. They found that solutions of alums of these elements reacted with sodium trinitride in a manner similar to that described for thorium by Dennis and Kortright (*Zeit. Anorg. Chem.*, vi., 35; *Am. Chem. Journ.*, xvi., 79), and by Dennis (*Journ. Am. Chem. Soc.*, xviii., 947), who found that thorium is quantitatively precipitated from solution by the addition of potassium trinitride on boiling. These three elements, as well as the thorium, separate under this treatment in the form of hydroxides. A new basic trinitride of chromium (ratio, $\text{Cr} : \text{N}_3$) was prepared. Zirconium was found to be precipitated quantitatively as hydroxide, even in the cold, by the addition of sodium trinitride to a solution of zirconium sulphate. With yttrium, lanthanum, cerium, and didymium they obtained basic salts in which two nitride groups were joined to each atom of the element in question. By boiling a solution of uranyl nitrate after treatment with sodium trinitride they effected a quantitative separation of uranyl hydroxide. Using the method of precipitation with alcohol and ether, they confirmed the results of Curtius and Rissom by preparing the basic trinitride of manganese, and also prepared the neutral trinitride of nickel, $\text{NiN}_6\cdot\text{aq}$. Attempts were made to isolate the trinitrides of arsenic and antimony, but without success.

In 1900, Hantzsch (*Ber.*, xxxiii., 522) prepared a trinitride of iodine, IN_3 , by the action of a solution of iodine in benzene or ether upon silver trinitride.

A crystallographic study of several of the inorganic trinitrides was made by Gill (*Journ. Am. Chem. Soc.*, xx., 225; xviii., 970; *Zeit. Anorg. Chem.*, xvii., 18) and by Rosenbusch (*Journ. Prakt. Chem.*, lviii., 261; *Z. Krystall.*, xxxiii., 99).

Curtius and his students have prepared a large number of the compounds of hydronitric acid with organic acids, the compound carbonyl trinitride (carbazine), $\text{CO(N}_3)_2$, is of especial interest to the inorganic chemist because of its analogy to carbonyl chloride. Curtius (*Ber.*, xxvii., 2684) prepared this compound by the action of sodium nitrite

upon the hydrochloric acid salt of carbonyl hydrazide, $\text{CO(NH.NH}_2\cdot\text{HCl)}_2$. Pommerehne (*Arch. Pharm.*, cxxxvi., 479) has prepared several compounds of hydronitric acid with organic bases. For information with respect to these compounds, and for further details concerning the inorganic compounds mentioned above, the reader is referred to the original papers, or to the recent work of Dr. Leopold Spiegel, "Der Stickstoff und Seine Wichtigsten Verbindungen."

(To be continued.)

SILICA DETERMINATIONS.

By HARRISON EVERETT ASHLEY,
Chemist Homer Loughlin China Co.

THE recent discussion of the need of two evaporations to dryness in order to separate silica completely from solution has had reference to two classes of solutions:—

Class I.—The acidified extract of an alkaline fusion (the most general case).

Class II.—The acid solution of a completely soluble silicate mixture (cements).

In iron-ore analysis, as frequently practised, two further cases occur.

Class III.—The hydrochloric acid extract of the ore leaves a portion of the silica as an insoluble residue.

Class IV.—The hydrochloric acid extract of the ore leaves all of the silica as an insoluble residue.

The extract of Class III. must be evaporated to dryness and filtered, once or twice according to the amount of soluble silica and the skill of the analyst. The additional silica so obtained is put with the original insoluble residue, ignited, and weighed, then corrected by evaporation with hydrofluoric and sulphuric acids, ignition and weighing. If desirable, the non-volatile residue may be fused with a very small amount of sodium carbonate, and added to the main extract.

The silicious residue in the Class IV. may be at once ignited and weighed, and the gross weight corrected by treatment with hydrofluoric and sulphuric acids. Thus, an ore that is found to fall in this class requires no evaporation to dryness for the silica determination.

The procedures in these two last cases save much time, and keep down the amount of sodium salts in solution.

I have treated high grade limestones similarly. After dissolving in hydrochloric acid, evaporating to dryness, taking up with hydrochloric acid, and filtering, and repeating this procedure, about one-half the insoluble residue is silica. Mr. S. V. Peppel, formerly of the Ohio Geological Survey, informs me that some time ago, in seeking a rapid commercial method, he attempted to apply the process to lower grade limestones, but found the loss of weight with the hydrofluoric and sulphuric acid treatment greater than the amount of silica present.—*The Chemical Engineer*, No. 1, November, 1904.

Preparation of Aurous Iodide by the Action of Iodine on Gold.—Fernand Meyer.—At ordinary temperatures pure and dry iodine has no action upon gold, and aurous iodide does not decompose in a vacuum. Between 50° and its melting-point pure and dry iodine does combine with gold with the production of amorphous iodide. At the melting-point of iodine, and above, crystallised aurous iodide is obtained. The direct action is always limited by decomposition of the iodide obtained; but the latter can be obtained pure by using excess of iodine and separating the iodine from the iodide by heating to 30° . In the presence of water, in a closed vessel, iodine and gold form aurous iodide; but if the iodine can escape, aurous iodide is completely decomposed by water or damp air.—*Comptes Rendus*, cxxxix., No. 19.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, November 3rd, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

(Concluded from p. 265).

173. "Note on the Influence of certain Salts and Organic Substances on the Oxidation of Guaiacum." By Miss EDITH GERTRUDE WILLCOCK.

The author has investigated the influence of various salts on the oxidation of guaiacum with hydrogen peroxide by determining the time necessary to produce a standard blue tint when the conditions were so adjusted that the concentration of guaiacum, peroxide, and salt, and the temperature were the same throughout the series.

It was found that the oxidation was accelerated by the chlorides of ammonium, lithium, potassium, barium, iron, and aluminium, the bromides of sodium and potassium, potassium iodide, sodium fluoride, and potassium nitrite; whereas the nitrates of ammonium, potassium, and barium, and the sulphates of sodium, potassium, and magnesium had no appreciable influence.

These results show (1) that the influence of the salt is determined by the nature of the anion, and (2) that the halogen salts as a group accelerate the oxidation.

Of the salts examined, those of the halogens alone showed a true accelerating action, for although potassium nitrite certainly accelerates the oxidation of guaiacum by hydrogen peroxide, yet as it will itself oxidise this resin in the absence of the peroxide its influence is not comparable with that of the salts which have no independent oxidising action; this remark also applies to ferric chloride.

A comparison of the salts of the halogens among themselves showed that the iodides have the greatest accelerating action, the effect of the others diminishing in the following order, namely, bromides, chlorides, and fluorides. The position of the iodides in the list may be connected with the oxidising action of hydrogen peroxide on these salts.

Salts, such as aluminium chloride and sodium fluoride, which form acid solutions, have a relatively feeble accelerating power.

Ordinary "pure" aluminium chloride readily oxidises guaiacum even in the absence of peroxide, but a specially purified sample of the salt had no independent oxidising action whatever, and it increased the rate of oxidation by hydrogen peroxide only very slightly. The activity of commercial aluminium chloride is probably due to the presence of ferric chloride.

The acids of the acetic series have no accelerating action, but the metallic salts of the lower members of the series have a slight influence, due probably to the fact that they are hydrolysed by water into free acid and base. Carbohydrates and proteids have no action.

Formaldehyde is commonly described as oxidising guaiacum, but this effect is probably due to impurities. The commercial product is an active oxidiser, turning guaiacum blue even in the absence of hydrogen peroxide, but pure formaldehyde, freshly prepared by the distillation of paraformaldehyde, has no action whatever.

Commercial glycerol readily oxidises guaiacum, turning the resin blue immediately, but in this case also the action seems to be due to impurities, for when freshly distilled under diminished pressure in the dark it has no effect by itself, although, like methyl and ethyl alcohols and ethylene glycol, it assists the accelerating action of the metallic haloids at the ordinary temperature (15–25°). These substances, however, at 50–70° all exert a retarding influence, and this may be due to some absorption of the available oxygen by the alcohol.

The carbohydrates dextrose, lævulose, sucrose, maltose, dextrin, starch, glycogen, and mastic decrease the

accelerating action of the salts, and the proteid globulin has the same action.

The action of carbohydrates and proteids (globulins) in diminishing the accelerating power of salts is probably due to the fact that the organic substance, being itself oxidisable, absorbs a part of the oxygen which is liberated, and also to its influence on the degree of dissociation of the salt (compare Walker and Hamby, *Trans.*, 1897, lxxi., 61).

The effect of sucrose on the electrical conductivity of sodium chloride has been measured by Mr. Hardy, who found that the presence of 16 per cent of this sugar in a normal solution of the salt diminished the electrical conductivity by 23 per cent (compare *Journ. Physiol.*, 1903, xxix., 26).

The accelerating action of the alcohols is adequately explained by their influence on the solubility of the guaiacum. When an alcoholic solution of the resin is added to water, precipitation occurs, but on the addition of more of the alcohol the precipitate re-dissolves. This was found to be the case with all the alcohols examined except mannitol, and this substance alone failed to accelerate the oxidation of the guaiacum.

174. "Note on the Influence of Potassium Persulphate on the Estimation of Hydrogen Peroxide." By JOHN ALBERT NEWTON FRIEND.

It was shown in a recent communication (*Trans.*, 1904, lxxxv., 597) that in ordinary circumstances a correct estimate of hydrogen peroxide is not obtained by titration with potassium permanganate. The author now shows that for every molecule of peroxide not accounted for a molecule of persulphate disappears. This observation suggests that the reaction $H_2O_2 + K_2S_2O_8 \rightarrow K_2SO_4 + H_2SO_4 + O_2$ probably takes place, this change being catalytically accelerated by some oxide of manganese formed during titration.

175. "The Influence of Sunlight on the Dissolution of Gold in Aqueous Potassium Cyanide." By WILLIAM ARTHUR CALDECOTT.

The fact that the formation of potassium thiocyanate in aqueous solution, under the conditions indicated by the equation $PbS + KCy + O \rightarrow PbO + KCNS$, is accelerated by bright sunlight, was noted some years ago by Bettel and Feldtmann (*Proc. Chem. Metallurg. Soc. S. Africa*, 1896, i., 267). In a paper published last year (*Journ. Chem. Metallurg. Soc. S. Africa*, 1903, iv., 51) by E. H. Johnson and the author, the analogy between potassium aurocyanide and potassium thiocyanate with regard to their formation and reduction was discussed.

The following experiments were carried out with the view of ascertaining whether sunlight accelerated the formation of potassium aurocyanide, as well as that of potassium thiocyanate.

A strip of gold foil weighing 832.5 milligrams, and having a total superficial area of 852 sq. m.m. was immersed in a 0.5 per cent potassium cyanide solution, contained in a clear glass litre bottle at about 19°. In another similar glass vessel, coated with three layers of black varnish, was placed a corresponding amount of the potassium cyanide solution and a strip of gold foil weighing 900 milligrams, but with a superficial area equal to that of the other strip. The two bottles were then exposed to direct sunlight for about five and a-half hours daily during five days, the loss of weight of the gold foil strips was noted, the maximum temperatures of the solutions being recorded daily. The results were as follows:—

	The clear bottle.		The blackened bottle.	
	Gold dissolved in milligrams.	Temp.	Gold dissolved in milligrams.	Temp.
1st day ..	25.5	30	20.0	40
2nd day ..	21.0	34	17.0	38
3rd day ..	28.0	34	20.0	38
4th day ..	27.0	37	17.0	40
5th day ..	32.0	30	19.0	43
Daily average ..	26.7	36	18.6	39.8

This table shows that the rate of dissolution of the gold in the clear glass bottle was 43 per cent greater than that in the blackened vessel, although the temperature of the solution was on an average 3.8° lower than in the former case.

The lately published researches of Berthelot (*Comptes Rendus*, 1904, cxxix., 169) indicate that the absorption of oxygen by aqueous potassium cyanide is accelerated by sunlight. The greater rapidity with which gold dissolves in potassium cyanide solution in bright sunlight may hence be considered as being due to the liberation of more nascent cyanogen, in proportion to the additional oxygen absorbed, with the consequent increased formation of aurous cyanide.

176. "The Fractional Hydrolysis of Amygdalinic Acid, *iso*-Amygdalin." By HENRY DRYSDALE DAKIN.

As amygdalinic acid, prepared by the action of hot baryta solution on amygdalin, gives racemic mandelic acid on complete hydrolysis with acids, it is therefore probably a partially racemic substance, and may be considered as being the maltoside of inactive mandelic acid. On fractional hydrolysis, it was found that the mandelic acid set free in the earlier stages of the reaction was strongly dextrorotatory, whilst that liberated at a later stage was levorotatory. By repeated crystallisation of the magnesium salts and of the free acids derived from the products of hydrolysis, it was found possible to isolate both optically active varieties of mandelic acid in a pure state.

Starting from amygdalin, which on hydrolysis gives *l*-mandelic acid almost exclusively, it is thus possible to prepare both *d*- and *l*-mandelic acids without employing any additional optically active substance.

The production of an isomeric partially racemic amygdalin, as the result of the limited action of baryta solution on amygdalin, was suggested by J. W. Walker (*Trans.*, 1903, lxxxiii., 472), but efforts to isolate the substance were unsuccessful.

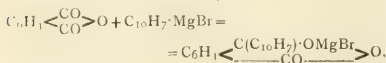
The substance has now been obtained in crystalline form, and its main properties have been investigated; it is very much more soluble in water and alcohol, has a much lower melting point, and a higher specific rotation than ordinary amygdalin. The close relationship between the two substances is shown by the fact that both are similarly attacked by the enzymes, emulsin and maltase.

The new substance gives amygdalinic acid and ammonia on treatment with alkali, whilst with concentrated acids it yields mandelic acid, glucose, and ammonia. The mandelic acid set free on complete hydrolysis with hydrochloric acid is distinctly dextrorotatory, whereas that derived from ordinary amygdalin is levorotatory. The suggested cause of this surprising result is that the two forms of which *iso*-amygdalin, as a partially racemic substance, may be assumed to be composed are hydrolysed at unequal rates, and that the form which is least readily hydrolysed undergoes progressive racemisation.

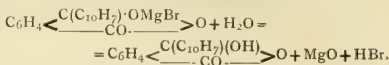
177. "The Effect of Anhydrides on Organo-magnesium Bromides. Part I. The Action of Phthalic Anhydride on Magnesium α -Naphthyl Bromide." By SAMUEL SHROWDER PICKLES and CHARLES WILZMANN.

Although Grignard's reaction has been extensively used for the production of hydrocarbons, alcohols, and acids from ketones and esters, the effect of this reaction on anhydrides does not seem to have been studied. With the object of discovering another method for the preparation of certain quinones and their derivatives, the magnesium reaction was tried with magnesium α -naphthyl bromide and phthalic anhydride. The course of the reaction may be expressed as follows:—

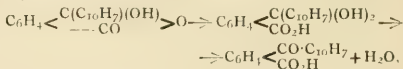
1. Formation of additive compound:—



2. Action of water and dilute acid:—



3. Further action of water:—



the product of the reaction being a keto-acid, in this case, α -naphthyl-*o*-benzoic acid.

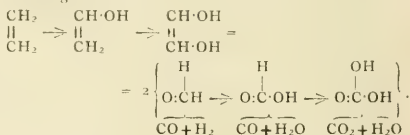
Such acids, on treatment with strong sulphuric acid, pass almost at once into quinones, the foregoing acid, for example, yielding naphthanthraquinone.

Subsequent experiments have shown that the above reaction is capable of general application. Thus, using phthalic anhydride and bromobenzene, the authors have obtained benzoyl-*o*-benzoic acid and anthraquinone, and with phthalic anhydride and β -bromonaphthalene they have obtained β -naphthyl-*o*-benzoic acid and naphthacene-quinone.

Experiments are now being carried out in the aliphatic series with succinic anhydride and various fatty bromides.

178. "The Combustion of Ethylene." By WILLIAM ARTHUR BONE and RICHARD VERNON WHEELER.

The combustion of ethylene appears to be essentially a process of hydroxylation, that is, oxygen initially enters the hydrocarbon and is distributed between the carbon and hydrogen, giving rise to hydroxylated molecules, which sooner or later, according to the rapidity of the process, undergo thermal decompositions into simpler products. The stages in the combustion are represented by the following scheme:—



The more salient features of the experiments may be summarised as follows:—

1. There is no preferential combustion of either carbon or hydrogen when ethylene interacts with a quantity of oxygen insufficient to burn it completely to steam and oxides of carbon. The separation of carbon or hydrogen, when it does occur, is to be entirely ascribed to secondary thermal decompositions.

2. Formaldehyde is the most prominent intermediate oxidation product, and at low temperatures its formation is probably preceded by that of a less oxygenated product.

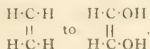
3. The formation of aldehydes precedes that of steam and oxides of carbon.

4. The stage in the combustion process at which secondary decompositions set in is determined entirely by the temperature conditions. Below the ignition point, such changes do not come into play to any appreciable extent until the stage corresponding with the formation of formic acid is reached. The greater part of this substance then decomposes into carbon monoxide and steam, whilst the remainder is further oxidised to carbonic acid, which in turn breaks down into carbon dioxide and steam. Above the ignition point, the formaldehyde produced rapidly decomposes into carbon monoxide and hydrogen.

5. There is no separation of carbon or liberation of acetylene, even in the explosive combustion of ethylene, except when the oxygen present is insufficient to burn the hydrocarbon to formaldehyde. In such circumstances the excess of ethylene is thermally decomposed, yielding carbon, hydrogen, methane, and traces of

acetylene. Some evidence was obtained under suitable conditions of the transformation of the initial product, $\text{CH}_2\text{CH}:\text{OH}$, into the isomeric acetaldehyde, which is then independently oxidised to carbon monoxide, water, and formaldehyde, as proved in a previous paper.

The authors have not yet decided whether at low temperatures the oxygen is conveyed to the hydrocarbon directly or indirectly, but at high temperatures, as, for example, in the explosion wave, it is believed that there is a direct passage from



as the result of collisions between single molecules of ethylene and oxygen.

179. "The Decomposition of Methylcarbamide." By CHARLES EDWARD FAWCETT.

This investigation has been conducted on similar lines to that on carbamide (*Zeit. Physical. Chem.*, 1902, xli., 601), and it is found that the mechanism of the decomposition is precisely similar in the two cases, so that the theory put forward to explain the decomposition of carbamide is also applicable in the present instance.

The decomposition of methylcarbamide by acids is due to a transformation of the methylcarbamide into methylamine cyanate, which is subsequently decomposed by the acid. The initial transformation is a reaction of the first order, and the velocity coefficient at 99° is almost exactly one-half that of carbamide. In these experiments it is only the free methylcarbamide which represents the active concentration of substance decomposing at any instant. A direct hydrolysis is brought about only very slightly even by very concentrated alkali, and the reaction with pure water is very much slower than is the case with carbamide.

180. "Position Isomerism and Optical Activity: the Methyl and Ethyl Esters of Di-*o*-, *m*-, and *p*-Nitrobenzoyl-tartaric Acids." By PERCY FARADAY FRANKLAND and JOHN HARGRE.

The authors describe the preparation and properties of the six esters in question, which were obtained by the action of the three isomeric nitrobenzoyl chlorides on methyl and ethyl tartarates respectively. The rotation of each was determined in the fused state, and over a wide range of temperature, in some cases from 15° to 180° . All these compounds, like the corresponding dibenzoyl- and ditoluyll-tartrates, are strongly levorotatory. The *p*- and *m*-nitrobenzoyl groups were found to exercise a very great rotatory effect, the molecular rotations of the diethyldi-*p*- and di-*m*-nitrobenzoyltartrates and of the dimethyl di-*p*-nitrobenzoyltartrate being considerably in excess of those exhibited by the corresponding dibenzoyl- and ditoluyll-tartrates. The dimethyl di-*m*-nitrobenzoyltartrate, on the other hand, exhibited a molecular rotation, which, although considerably greater than that of dimethyl dibenzoyltartrate, was almost identical with that of dimethyl di-*m*-toluylltartrate.

The *o*-nitrobenzoyl group behaved in an altogether exceptional manner, its relative rotatory influence being entirely dependent on the temperature. Thus it has been previously shown by one of the authors (P. Frankland and Wharton, *Trans.*, 1896, lxi., 1591) that the rotatory effect of the *o*-toluyll group is inferior to that of the benzoyl group, and it would have been anticipated, therefore, that the *o*-nitrobenzoyl radicle should exert a still smaller effect; this was actually found to be the case above 130° , but with fall of temperature its rotatory effect so rapidly increases that at 15° the latter proved to be even greater than that of the *p*-nitrobenzoyl group. This abnormal behaviour of the *o*-nitrobenzoyl group, which was only fully studied in the case of the ethyl compound, was thus limited to the superheated state, the melting-point of diethyl di-*o*-nitrobenzoyltartrate being 143° . This melting-point, again, is exceptional in being considerably higher than

that of the meta- (95.8°) and that of the para- (124.5°) compounds respectively.

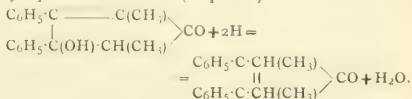
The rotation of all these compounds is very sensitive to temperature, diminishing in every case as the latter rises, much the largest temperature-coefficient being possessed by the ortho-compound.

181. "The Action of Nitrogen Sulphide on Organic Substances." (Part II.) By FRANCIS ERNEST FRANCIS and OLIVER CHARLES MINTY DAVIS.

The action of nitrogen sulphide on anisaldehyde gives rise to tri-*p*-methoxycyanidine and anisamidine sulphate, which are isolated by taking advantage of their solubilities in benzene and water respectively. An insoluble derivative of anisamidine, containing sulphur, is also produced which is very stable towards alkalis, but yields anisoylanisamidine on treatment with strong acids.

182. "Reduction Products of α, β -Dimethylanthracetonebenzil, and Condensation Products of Benzaldehydes with Ketones." By FRANCIS ROBERT JAPP and WILLIAM MAITLAND.

When α, β -dimethylanthracetonebenzil is boiled for a few minutes with fuming hydriodic acid, it is reduced to a cyclopentenone derivative (m. p. 122°):—

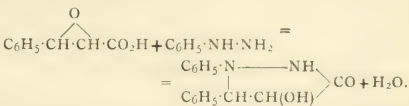


This compound is identical with that which Vorländer and Wilcke (*Ber.*, 1898, xxxi., 1877) obtained by the action of hydrogen chloride on dimethyldiphenyltetrahydro- γ -pyrone, but which they erroneously regard as dibenzylidenediethylketone. By further reduction with hydriodic acid, it yields the corresponding cyclopentanone derivative.

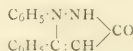
The authors have prepared various alkyl derivatives of tetrahydro- γ -pyrone by the usual method of condensing benzaldehyde with aliphatic ketones, and have studied their reactions, especially with the view of obtaining cyclopentenone derivatives.

183. "Interaction of Sodium Phenylglycidate with Phenylhydrazine." By FRANCIS ROBERT JAPP and WILLIAM MAITLAND.

When sodium phenylglycidate is heated with phenylhydrazine in alcoholic solution at 100° , 4-hydroxy-1:5-diphenyl-3-pyrazolidone (m. p. 173.5°) is obtained in the form of its sodium salt:—



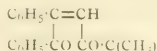
By the action of heat or of dehydrating agents hydroxydiphenylpyrazolidone is converted into 1:5-diphenyl-3-pyrazolone,—



(m. p. 252°), previously obtained by Knorr (*Ber.*, 1887, xx., 1107) by distilling cinnamoylphenylhydrazine.

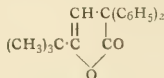
184. " α -Benzoyl-3-trimethacetylstyrene." By FRANCIS ROBERT JAPP and WILLIAM MAITLAND.

The authors have obtained α -benzoyl-3-trimethacetylstyrene,—

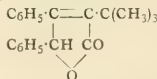


(m. p. 115°), by the action of potassium hydroxide on a mixture of benzil and methyl *tert*-butyl ketone. In its reactions, it closely resembles α, β -dibenzoylstyrene (Japp and

Klingemann, *Trans.*, 1890, lvii., 662, except that, on heating, it is converted into a mixture of two isomeric crotonolactones.—



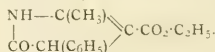
(m. p. 150°) and—



185. "Olefinic Ketonic Compounds." By SIEGFRIED RUHEMANN.

Rabe (*Ber.*, 1902, xxxv., 3947) stated that the additive compound of aniline and ethyl benzylideneacetoacetate melted at 78° instead of at 105° (erroneously printed as 103°) as found by Ruhemann and Watson (*Trans.*, 1904, lxxxv., 1170). On re-examination, it was found that the melting-point could be raised to 106 – 107° , which closely agreed with that given by Francis (*Ber.*, 1903, xxxvi., 937) for the substance he obtained by combining benzylideneaniline with ethyl acetoacetate.

The author also examined the action of potassium cyanide on benzylideneacetylacetone and ethyl benzylideneacetoacetate respectively, and found that in the first case cyanobenzylacetylacetone, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{CH}(\text{CO} \cdot \text{CH}_3)_2$ (m. p. 127 – 128°), and, in the other, ethyl cyanobenzylacetoacetate, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{CH}(\text{CO} \cdot \text{CH}_3) \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$, are produced. On hydrolysis with caustic potash, the former nitrile furnishes phenylacetylpropionic acid $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, whilst ethyl cyanobenzylacetoacetate yields a mixture of phenylacetylpropionic and phenylsuccinic acids. Under the influence of concentrated sulphuric acid, cyanobenzylacetylacetone is transformed into phenylacetylpropionic acid, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}(\text{CO} \cdot \text{CH}_3)_2$ (m. p. 149 – 150°); ethyl cyanobenzylacetoacetate, on the other hand, furnishes the dihydropyrene derivative,—



The mode of formation and the properties of cinnamylideneacetylacetone, $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}(\text{CO} \cdot \text{CH}_3)_2$ (m. p. 103 – 104°), are also described. This di-olefinic ketone, on exposure to light, undergoes a change similar to that occurring in the case of cinnamylidenemalonate (Liebermann, *Ber.*, 1895, xxviii., 1440; Riiber, *Ber.*, 1902, xxxv., 2411), and yields a colourless substance (m. p. 158 – 159°) which has double the molecular weight of cinnamylideneacetylacetone. These two compounds are still under examination.

186. "Δ^o Oleic Acid." By HENRY RONDEL LE SUEUR.

In a former communication (*Trans.*, 1904, lxxxv., 827), the author stated that he was engaged in the preparation of an isomeride of oleic acid containing the double linking between the α- and β-carbon atoms, and, although the work is not complete, the appearance of a paper by G. Ponzio (*Gazzetta*, 1904, xxiv., [2], 77; *Chem. Centr.*, 1904, ii., 691) on the same subject necessitates the publication of the results so far obtained.

Δ^o-Oleic acid, $\text{C}_{15}\text{H}_{31} \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H}$, obtained by the action of alcoholic potash on α-bromostearic acid, crystallises from light petroleum in long flat needles melting at 58 – 59° ; its ethyl ester melts at 25 – 26° . The acid, on oxidation with potassium permanganate, yields αβ-dihydroxystearic acid melting at 126° , which on further oxidation yields palmitic acid, thereby proving the position of the double linking.

187. "Action of Magnesium Alkyl Halides on Derivatives of Camphor." By MARTIN ONSLOW FORSTER.

The action of magnesium alkyl halides on derivatives of

camphor has been always normal, and several interesting changes have been observed.

The compound, $\text{C}_{12}\text{H}_{22}\text{O}_2$, from camphorquinone and magnesium methiodide is a volatile colourless compound, dissolving readily in organic media and very sparingly in water, from which it crystallises in minute transparent prisms and needles melting at 132° . A 2 per cent solution in absolute alcohol is optically inactive.

The compound, $\text{C}_{11}\text{H}_{19}\text{O}_2\text{N}$, from isonitrosocamphor and magnesium methiodide is soluble in acids and alkalis, forming colourless solutions; it separates from boiling water as a crystalline powder, and melts at 180° .

The compound, $\text{C}_{11}\text{H}_{19}\text{O}_3\text{N}$, from nitrocarnphor and magnesium methiodide is insoluble in sodium carbonate solution, but dissolves in aqueous sodium hydroxide; it crystallises from petroleum in lustrous leaflets melting at 83° .

The compound from hydroxymethylenecamphor and magnesium methiodide is a colourless fragrant oil which boils at $234^\circ/765$ m.m., has sp. gr. 0.9639, and $[\alpha]_D^{20}$ 170 – 8° . It is insoluble in aqueous sodium hydroxide, and gives no colouration with ethereal ferric chloride.

188. "Sulphonchloroalkylamines." By FREDERICK DANIEL CHATTAWAY.

In the course of an investigation of nitrogen halogen derivatives of the sulphonamides, a number of compounds yielded by various methyl, ethyl, and benzyl derivatives of the sulphonamides have been obtained. All the sulphonalkylamides are readily converted by a solution of hypochlorous acid into the corresponding chloroamides, $\text{RSO}_2 \cdot \text{NHR}' + \text{HOCl} = \text{RSO}_2 \cdot \text{NClR}' + \text{H}_2\text{O}$. Those containing methyl and ethyl groups are comparatively stable, whereas those in which benzyl occurs undergo spontaneous decomposition after a few hours; even when kept in dry air, chlorine and hydrogen chloride are liberated, while a pungent odour, resembling that of benzaldehyde, becomes apparent. When rapidly heated, they all decompose with evolution of gas, but without explosion. Like the sulphonchloroamides, they are very reactive, and promise to be of considerable value in the synthesis of secondary amines containing different alkyl groups.

The following compounds are typical examples of a long series of these substances which have been prepared:—Benzenesulphonchloromethylamide, $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_3$, colourless, short rhombs, m. p. 81° ; benzenesulphonchloroethylamide, $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_2\text{H}_5$, colourless plates, m. p. 52° ; benzenesulphonchlorobenzylamide, $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$, colourless, slender prisms, m. p. 109° ; *p*-toluenesulphonchloromethylamide, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_3$, colourless prisms, m. p. 82° ; *m*-nitrobenzenesulphonchloromethylamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_3$, pale yellow four-sided plates, m. p. 136° ; α-naphthalenesulphonchloromethylamide, $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_3$, colourless six-sided prisms, m. p. 78° ; α-naphthalenesulphonchlorobenzylamide, $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$, very pale yellow prisms, m. p. 94° ; β-naphthalenesulphonchloromethylamide, colourless prisms, m. p. 91° ; β-naphthalenesulphonchloropropylamide, $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_3\text{H}_7$, colourless plates, m. p. 86° .

PHYSICAL SOCIETY.

Ordinary Meeting, November 25th, 1904.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A PAPER ON "The Measurement of Small Differences of Phase" was read by Dr. W. E. SUMPNER.

Hitherto, in order to measure the differences of phase between alternating-current quantities, it has been necessary to use some method involving the simultaneous reading of three deflectional instruments, such as the wattmeter method, or the three-voltmeter method either in its original or in some modified form. These methods

cannot be successfully applied when the phase-differences to be determined are small. The author describes new voltmeter methods which may be used for the purpose, and gives the results of a number of measurements on alternating-current plant. Difficulties arising in the measurement of very small alternating-current voltages are overcome by rectifying the voltages so as to utilise sensitive direct-current instruments. The paper gives the results of some tests on two transformers of 3 kilowatt capacity intended to work between voltages of 100 and 2000, and with currents of 100 cycles per second. One transformer was used to step up the volts from V_1 to V_2 , the other to step down from V_2 to V_3 . It was found that the phase-difference between V_1 and V_3 for a non-inductive load increases regularly with the current. For an inductive load there is a sharply defined minimum at low power factor. The author suggested that points on one side of the minimum corresponded to a lag, and points on the other side to a lead of the current on the voltage in the primary circuit.

Dr. A. HAY congratulated the author, and said that the determination of power factors was a matter of importance. He had found that alternators tested with water resistances gave better results than when tested with lamps. The phase-differences between the volts and the amperes in the water resistances were generally greater than those indicated by Dr. Sumpner. He asked the author what current-density he used, and pointed out that the result would depend upon the current-density at the electrodes. A minimum phase-difference could be obtained by loading up the secondary of an ordinary transformer, and was due to an increase in the power factor up to a certain point and then a decrease. We were dealing with lag in both cases.

Mr. A. CAMPBELL said that some years ago (*Journ. Inst. Elec. Engineers*, April, 1901) he published a description of the method of measuring a phase-difference, close to 180° , between two independent voltages by the first method mentioned by Dr. Sumpner, viz., by shunting the larger by a high resistance, picking off from it a part as nearly as possible equal to the other, and measuring the difference resultant. A test on a small transformer gave a phase-difference of about $(180-0.15^\circ)$. Dr. Sumpner, however, has considerably improved the method; he ensures the sufficient equality of the components by adjusting until the resultant is a minimum—a simple and beautiful device. In his discussion of the three-voltmeter method, Dr. Sumpner assumes that three instruments are necessary. Mr. Campbell has found that in many cases a single instrument with a quick change-over switch is quite sufficient provided a number of readings are taken in rotation and averages obtained. With respect to Dr. Sumpner's method of measuring small alternating voltages by rectifying them, although it might give good results when the wave-form was known, he thought that in the very cases where such measurements were wanted the wave-form was not known. Small differences of "power" phase may be as much due to small differences in wave-form as to small displacements of similar waves: thus the "difference" resultant is probably nearly always of very uncertain wave-form.

Mr. T. H. BLAKESLEY expressed his interest in the paper, and said that many years ago he had made use of commutation in order to work with direct-current instruments. He had used a high-resistance galvanometer, and found that not only the self-induction but also the capacity of the coils had to be eliminated.

Mr. W. DUDELL supported Mr. Campbell in his contention that small differences of "power" phase might be due to small differences in wave-form. He had used water resistances in testing large alternators, but had never found any phase-difference between the voltage and the current. He had usually worked with high voltages, so that condenser effects due to polarisation (of the order of one volt) would have little effect.

Dr. C. V. DRYSDALE said he had given a good deal of attention to the measurement of small phase-differences,

and had found it advantageous to measure the sine of the phase-difference instead of the cosine. This could be accomplished by putting a condenser in series with the pressure circuit of a wattmeter so as to produce a phase displacement of nearly 90° . In these circumstances he had previously shown that with ordinary conditions the watts were equal to the wattmeter reading plus a constant multiplied by the sine of the angle of phase-difference. When, as was usually the case, $\sin \theta$ was nearly equal to unity it was only necessary to add a constant to the wattmeter reading.

Dr. W. E. SUMPNER, in reply to Prof. Hay, said he had worked with low current-densities and was unable to say what would happen if the current-density was increased. With regard to rectification he was aware of the effect of the shape of the wave. He had made experiments with currents of very different wave-forms, and in his opinion only about 20 per cent of the observed results could be due to any alteration in the form of the wave. His methods were suggested as a means of getting an approximate value of very small phase-differences, which could not be determined in other ways. The difficulties referred to by Mr. Blakesley were not encountered, as he had worked with a moving coil galvanometer of small capacity and self-induction. He was afraid that the observations of Dr. Drysdale raised questions which it would take too long to discuss at the present meeting.

A paper "On the Curvature-method of Teaching Geometrical Optics," by Dr. C. V. DRYSDALE, was postponed, at the author's request, in order that advance proofs might be in the hands of Fellows before the reading of the paper.

Dr. C. V. DRYSDALE then exhibited and described apparatus for the direct determination of the curvatures of small lenses, such as the objectives of microscopes. Parallel light from a distant source falls upon a plane unsilvered mirror inclined at an angle of 45° . Some of the light is reflected and brought to a focus by an ordinary convex lens. The surface to be tested is placed at this point, and the reflected rays proceed as if they had come from a point on the surface. They pass through the plate glass into a telescope focussed for parallel rays, and an observer sees an image of the distant source. If the surface is convex and is brought nearer to the lens, then, when it reaches such a position that its centre of curvature is at the focus of the rays emerging from the lens, the light will again retrace its former path and a distinct image of the source will be seen in the telescope. In order to obtain the two images the surface has therefore been moved through a distance equal to its radius of curvature. If the surface is concave it must be moved away from the lens. Dr. Drysdale showed how the method could be carried out by means of an auxiliary piece fitted to an ordinary microscope. He also described a method of testing the spherical and chromatic aberration of microscopic objectives. Light from a distant point is partially reflected by means of a piece of plate-glass down the axis of the microscope. In passing out of the objective it is brought to a focus upon a mirror and retraces its path along the axis of the instrument until it reaches the plate-glass. This it passes through, and by means of a telescope an observer can view the distant source. The light having passed twice through the lens to be investigated, the effects of chromatic and spherical aberration are doubled and at the same time the effect of coma is eliminated.

Prof. S. P. THOMPSON then gave an Exhibition of Specimens of Crystals showing the phenomenon of Luminous Rings.

He said it was well known that when a source of light was viewed through certain samples of calc-spar the field of vision contained two luminous rings each of which passed through the image of the luminous point. The subject had been investigated by Dr. Johnstone Stoney, who had attributed the phenomenon to a minute tubular structure in the crystal. There were, however, certain crystals which when cut in the ordinary way across the

axis and used to view a distant source of light, exhibited a single luminous ring passing through the image of the source. Looking down the axis of the crystals no ring is visible, but on tilting it a ring can be seen in the direction of the tilt which grows in diameter as the tilt is increased. So far as he knew no explanation of these phenomena had been offered. At the meeting, a piece of calc-spar showing the two rings and pieces of beryl and tourmaline showing the single ring were exhibited.

A paper "On a Rapid Method of Approximate Harmonic Analysis," by Prof. S. P. THOMPSON, was postponed.

Several of the Laboratories of the College were open to the inspection of Fellows, and apparatus was exhibited by Prof. Dalby, Mr. Darling, Dr. Drysdale, and Prof. Thompson.

ROYAL SOCIETY OF NEW SOUTH WALES.

Wednesday, October 5th, 1904.

C. O. BURGE, M.Inst.C.E., President, in the Chair.

THE following papers were read:—

"Preliminary Observations on Radio-activity and the Occurrence of Radium in Australian Minerals," by D. MAWSON, B.E., Junior Demonstrator, and T. H. LABY, Acting-Demonstrator of Chemistry in the University of Sydney. (Communicated by Prof. T. W. E. DAVID, B.A., F.R.S.)

A brief summary of observations on the radio-activity of minerals and occurrence of radium is given, showing that comparatively intense activity is only found associated in minerals with thorium and uranium. Bottwood and Strutt have independently shown that usually radium and uranium content are proportional. In these experiments the ionisation produced in an air gap was determined by measuring the saturation current across it, first with the mineral and then with black uranium oxide. Thus the activity compared to black uranium oxide was obtained. The presence of radium was looked for by Strutt's application of Rutherford and Soddy's discovery that radium gives off a radio-active gas, the emanation, which decays in activity to half its initial value in four days. A torbernite and euxenite were found highly active, but the specimens were too small to examine for radium. A Western Australian gadolinite, found by Professor Norman Collie to contain one bubble of helium in 10 grms., was expected to contain radium, but none could be detected. Twelve monazites were found radio-active; one, with double the average activity of the others, from Pilbarra, Western Australia, gave on heating the radium emanation; five monazite and zircon sands were also active. No relation between thorium contents and activity was found, which points to the presence of uranium.

Remarks were made by Prof. David, Prof. Pollock, Mr. G. H. Knibbs, Mr. F. B. Guthrie, Mr. W. M. Hamlet, the authors, and the President.

"The Flood Deposits of the Hunter and Hawkesbury Rivers," by Acting-Professor F. B. GUTHRIE, F.I.C., F.C.S., and Professor T. W. EDGEWORTH DAVID, B.A., F.R.S., F.G.S.

During the floods last July in the Hunter and Hawkesbury rivers, samples of the flood water as well as of the flood silt were collected, at the instance of the authors, by Mr. A. J. Prentice, B.A., of West Maitland, and Mr. W. W. H. Potts, the Principal of the Hawkesbury Agricultural College. Determinations made at the laboratory of the Department of Agriculture show the following to be the chemical composition of the silts:—

Silt from Hunter River Flood Water, West Maitland.

Insoluble in hydrochloric acid	Per cent.
Soluble in hydrochloric acid—	= 79.25
Oxide of iron and alumina (Fe_2O_3 and Al_2O_3)	= 10.02
Lime (CaO)	= 1.55
Potash (K_2O)	= 0.09
Phosphoric acid (P_2O_5)	= 0.18
Volatile matter	= 9.61
Nitrogen	= 0.084

Weight per acre, one foot in depth = 3,403,125 pounds.

Silt from Hawkesbury River Flood Water.

Insoluble in hydrochloric acid	= 89.96
Soluble in hydrochloric acid—	
Oxide of iron and alumina (Fe_2O_3 and Al_2O_3)	= 4.77
Lime (CaO)	= 0.49
Potash (K_2O)	= 0.12
Phosphoric acid (P_2O_5)	= 0.08
Volatile matter	= 4.68
Nitrogen	= 0.105

Weight per acre, one foot in depth = 3,307,332 pounds.

Mr. Prentice estimates the average depth of the last flood deposit of the Hunter to be about two inches. This would supply the land with a top dressing of fertilising constituents to the following amount per acre:—

	Pounds.
Lime	8791
Potash	510
Phosphoric acid	1020
Nitrogen	476

The data for estimating the thickness of silt deposited by the Hawkesbury river are less complete than those for the Hunter. On the assumption that the thickness was only one-twentieth of that deposited by the Hunter river, the silt of the Hawkesbury flood would weigh 27,561 pounds per acre, and would supply per acre:—

	Pounds.
Lime	135
Potash	33
Phosphoric acid	22
Nitrogen	29

A discussion was commenced by Mr. J. H. Maiden, Dr. R. Greig Smith, and Prof. F. B. Guthrie, but on the motion of Mr. C. A. Süssmilch it was postponed to the next meeting.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 18, October 31, 1904.

The Atomic Weight of Aluminium.—M. KOHN-ABREST.—Two methods were used for finding the atomic weight:—(1) The metal was treated with hydrochloric acid, and the hydrogen produced was led over red-hot copper oxide and weighed as water. The mean of several experiments gave 27.05 ($\text{H}=1$, $\text{O}=15.88$) as the atomic weight. (2) Aluminium was converted into alumina; the atomic weight by this method was 27.09. The specimens of aluminium used for the above experiments were carefully analysed.

Action of the Halogen Derivatives of the Tri- and Penta-valent Metalloids upon Alkyl Halogen Compounds.—V. AUGER.—Already noticed.

Tetrahydride and Decahydride of Naphthalene.—Henri Leroux.—An account is given of the properties of the 8-tetrahydride and of the substances produced by acting upon it with chlorine and bromine. The decahydride was obtained by hydrogenising the tetrahydride. It is a colourless liquid with an agreeable smell; it boils at at 187—188°, and is decomposed when heated with lime to a red heat, naphthalene being produced. It acts energetically with chlorine, and monochloro- ($C_{10}H_{17}Cl$) and dichloro- ($C_{10}H_{16}Cl_2$) derivatives are obtained.

The Oxidation of Methyl and Ethyl Alcohols at the Boiling-points of these Substances.—René Duchemin and Jacques Dourlen.—The object of these researches was to find why the burners of alcohol lamps deteriorate so rapidly. The authors have proved—(1) That certain alcohols, sold as neutral, and which do not redden litmus-paper, contain acid in sufficient quantity to be estimated by soda, using phenolphthalein as indicator. (2) Both methyl and ethyl alcohols, under certain conditions, at their boiling-points give rise to acid, the amount of which increases with the duration of the distillation.

The Action of the Chlorides of Phosphorus upon Aromatic Organo-magnesium Derivatives.—R. Sauvage.—The author has studied the action of the oxychloride of phosphorus upon phenyl-magnesium bromide, benzyl-magnesium chloride, and α -naphthyl-magnesium bromide. Compounds having the formulae $R_3\equiv P=O$ and $R_2=P\equiv O$ seem to be produced. The latter, when decomposed by water, yields $R_2=P\equiv O$.

The Tetraoxycyclohexane Rosanilines.—Jules Schmidlen.—A colourless oxalate of malachite green has been recently described by Lambrecht and Weil. This salt, when heated to 70°, loses four molecules of water and is transformed into the coloured oxalate of malachite green. The composition and properties of the colourless oxalate show that it is a tetraoxycyclohexane rosaniline. Its behaviour on heating is therefore a new confirmation of the theory that a benzene nucleus of carbinol passes through a hexahydrobenzene stage before being finally transformed into a quinone nucleus.

The Density of Nitrogen Monoxide and the Atomic Weight of Nitrogen.—Already noticed.

MISCELLANEOUS.

Gunning Victoria Jubilee Prize.—The Council of the Royal Society of Edinburgh at its recent meeting decided to award Professor Sir James Dewar, F.R.S., the Gunning Victoria Jubilee Prize for 1900—1904, for his researches on the liquefaction of gases, extending over the last quarter of a century, and on the chemical and physical properties of substances at low temperatures.

Institute of Chemistry.—*Examination in Biological Chemistry.*—The following Candidates passed:—*Fellow:* Robert Macfarlane Clark, B.Sc. (Glasgow). *Associates:* Francis William Frederick Arnaud, Henry Wulff Kinnersley, Louis John Ezekiel Riley. *Candidates for the Associateship:* Walter Augustus Handcock, Francis Richard Henley, M.A. (Oxon.).

The Formation of Formic Aldehyde in the Combustion of Tobacco.—M. A. Trillat.—Experiments show that aldehydes (chiefly formic) are produced by the combustion of tobacco; they do not exist in the free state, but immediately they are formed they combine with the nitrogen bases present.—*Comptes Rendus*, cxxxix., No. 19.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Society of Arts, 8. (Cantor Lectures). "Musica Wind Instruments," by David James Bleikley.
Society of Chemical Industry, 8. "Raschig's Theory of the Lead Chamber Process," and "Theory of the Action of Metals on Nitric Acid," by Dr. E. Divers.
"A Rapid and Accurate Method for the Estimation of Phosphorus in Iron Ores," by Llewellyn J. Davies.
"Fluoroscope for Comparing Substances under the Influence of Radium Rays," by C. S. Stanford Webster.
Royal Institution, 5. General Monthly Meeting.
WEDNESDAY, 7th.—Society of Arts, 8. "The International Exhibition at St. Louis, U.S.A.," by Walter F. Reid, F.I.C. &c.
THURSDAY, 8th.—Society of Arts, 4.30. "Burma," by Sir Frederic W. R. Fryer, K.C.S.I., late Lieut.-Governor of Burma.
FRIDAY, 9th.—Physicist, 8. "Rapid Method of Approximate Harmonic Analysis," by Prof. S. P. Thompson. "High-frequency Alternator," by W. Duddell. Exhibition of Experiments to show the retardation of the signalling current on 3500 miles of the Pacific Cable between Vancouver and Fanning Island. Exhibit of Ayrton-Mather Galvanometers, Universal Shunts and Electrostatic Instruments, a New Type of Wattmeter, a New Form of Inductionless Resistance, and of other Instruments.

GOVERNMENT GRANT to defray the expenses of Scientific Investigations. Applications for the year 1905 must be received at the Offices of the Royal Society not later than JANUARY 31 next, and must be made upon printed forms to be obtained from the Clerk to the Government Grant Committee, Royal Society, Burlington House, London, W.

READ HOLLIDAY & SONS, Ltd.,
Chemical Manufacturers,
HUDDERSFIELD,

Supply **PICRIC ACID** of the finest quality, complying with the British Government tests.

THE CHEMICAL NEWS AND JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	s.	d.
Five lines in column (about 10 words to line)	0	3 6
Each additional line	0	0 6
Whole column	1	15 0
Whole page	3	0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGTON ST.
LONDON, E.C.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

RECTIFIED SPIRIT

(SPIRITS OF WINE).

B.P. and higher strengths. Duty paid; or
Duty Free under Finance Act 1902.

METHYLATED SPIRIT

Special Quotations to large
Institutions.

BOOR & SON,
DISTILLERS SINCE 1750,
115-121 Tooley Street,
LONDON, S.E.

E. GEORGE & SONS,

BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.,

ARE OPEN TO PURCHASE Complete Sets
or short runs of the following:—*Chemical News*, *The Analyst*
Journal of the Chemical Society, 1848 to 1870, *Journal of the Society*
of Chemical Industry, or the Publications of any other English or
Foreign Learned and Scientific Societies.—Libraries Purchased.
Current Catalogue of General Literature sent on application.



Glew's Scintilloscope.

Brilliant Scintillations from PITCHBLEND,
Ra, Po, U, Th, or any source of Alpha-Rays.

A Welsbach mantle excites the extremely sensi-
tive transparent screen of the Scintilloscope.

Scintilloscope, complete, with 2 sensitive screens,
charged with Polonium and Pitchblende respec-
tively, in pocket case, 7/6 post free.

Pieces of Pitchblende, ground flat, with sensitive
screen attached, showing scintillations with any
strong pocket magnifier, from 7/6 each, post free.

Radium, &c. for
Lectures on hire.

F. H. GLEW, 156, Clapham Road, London, S.W.

Chemische Fabrik Eidelstedt,

ACETONE, Chemically and Tech. pure. METHYL-SPIRIT. WOOD NAPHTHA.

METHYLENE, Type Regie.

ACETON OIL.

&c.

Joh. Oswaldowski, Altona E.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS or IN CONCENTRATED SOLUTION.
FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.

LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.

MELTING & BOILING-POINT TABLES.

BY
THOMAS CARNELLEY,
D.Sc. (Lond.), B.Sc. (Vict.), F.C.S.,
Professor of Chemistry in University College, Dundee.
The Standard and only work upon the subject.
2 Vols. Ry. 4ts. 799 pp. 42s.

HARRISON & SONS, Pall Mall, London, S.W.

SECOND EDITION.

With Illustrations.

Price 2s. net (post free 2s. 1½d.)

Mme. CURIE'S Thesis
ON
RADIO-ACTIVE SUBSTANCES.
REPRINTED from the **CHEMICAL NEWS.**

CONTENTS.

Introduction.—Historical.—Chap. I. Radio-activity of
Uranium and Thorium; Radio-active Minerals.—Chap. II.
Method of Research.—Chap. III. Radiation of the New
Radio-active Substances.—Chap. IV. Communication of
Radio-activity to Substances Initially Inactive.—Nature
and Cause of the Phenomena of Radio-activity.

16, NEWCASTLE ST., FARRINGTON ST., E.C.

BRYAN CORCORAN LIM.

MILLSTONE BUILDERS,
WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.



Sole Makers of **MILBURN'S**
Patent Conoidal Stone Grinding Mills.
Especially suitable for certain materials, Water Dry.

Works and Warehouses: Back Church Lane.
Payrol Dept.: Basement of the Corn Exchange
31, MARK LANE, LONDON.

BIRKBECK COLLEGE,

Breams Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.

METALLURGY, MINING,
and ASSAYING .. G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board,
Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories.

ZINC

Suitable for the MARSH-BERZELIUS Test for ARSENIC,
As described in the "Report of the Inland Revenue Departmental
Committee on Arsenic-Testing."

LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.

Also WHITE LEAD, RED LEAD, CHEMICAL SHEET
LEAD and PIPE, LiTHARGE, SHOT, &c.

THE CHEMICAL NEWS.

VOL. XC., No. 2350.

THE ABSTRACTING OF CURRENT CHEMICAL LITERATURE.

By HUGH MARSHALL, D.Sc., F.R.S.

JUST as the rapid growth of the science of chemistry long since made it impossible for individual workers to take particular note of the literature of more than their own special departments, and rendered advisable the publication of short abstracts of original papers so as to enable workers to take a rapid review of the general literature, so now the continued expansion is beginning to make the provision of even highly condensed reports, in a thorough and efficient manner, a matter of considerable difficulty, or, at least, of considerable expense. The Berlin Chemical Society, which now publishes the well-known *Central-Blatt*, devoted entirely to abstracts of current chemical literature, has just issued a notice to the subscribers calling attention to the great increase of matter in the last few years, and intimating an increase of the price from twenty-eight to thirty-eight Marks per annum.

In view of the circumstances, it appears desirable that in the immediate future this whole question should be most carefully considered by the various bodies responsible for the publication of abstracts, and an endeavour made to arrive at some improved plan of dealing with it which would be efficient and economical. The following suggestions are made in the hope that they may lead to something being done in this direction.

The fact that the *indexing* of scientific literature generally is now being carried out on an international basis, immediately suggests the possibility of a somewhat similar method of international co-operation for abstracting chemical literature. At present, owing to the entire absence of co-operation, there is, even in one and the same language, a great amount of overlapping, and the same work is done repeatedly by different abstractors, and presumably has to be paid for in each case. For example, we have, in English, abstracts appearing in the *Journal of the Chemical Society*, the *Journal of the Society of Chemical Industry*, the *Journal of the American Chemical Society*, the *CHEMICAL NEWS*, and a number of others, some of them more or less specialised in character. An original paper may be, and often is, separately abstracted for every one, or nearly every one, of these periodicals; the same is the case with publications in other languages. There is, however, no special reason why a paper should be abstracted by more than one abstractor, provided the latter is expert at the work. Evidently, therefore (if we look at the matter in a sufficiently comprehensive way), there is room for a considerable saving of labour, and consequently of expense, and this might be effected in some such way as the following:—

For the sake of argument we may assume that the publication of abstracts in three languages (English, French, German) is desirable and sufficient; the actual number is immaterial. Let the leading chemical societies represented in these languages appoint an International Commission whose duty it would be to prepare a complete *résumé* of the current chemical literature of all countries, and either to publish the same themselves in the three languages, or, preferably, to arrange for its publication by separate national organisations. The Commission would appoint a large number of abstractors, each of whom would deal only with papers appearing in his own language, and relating to some department in which he was sufficiently versed, and it would also maintain a staff of skilled translators. Possibly the work of abstraction might be simplified

by authors themselves supplying abstracts of their papers, it being understood that, as regards length, such abstracts should not exceed a given percentage of the original paper. As soon as the abstracts were ready they would be forwarded to the central office of the Commission, where they would be classified and provided with reference data (year of publication of abstract, class, and running number in that class). The abstracts would then be translated as literally as might be into the three languages (or two of them if originally in one of the three), and thereafter the appropriate copies would be transmitted to the respective publishers in England, France, and Germany.

The expenses of the International Commission (*i.e.*, the cost of *preparing* the abstracts) would be shared by the various organisations responsible for its appointment, but each of the national publication committees would be itself responsible for the publication of its own edition, just as the Berlin Chemical Society is at present responsible for its own *Central-Blatt*. The abstracts would be issued separately, like the *Central-Blatt*, not conjointly with the publication of original papers, like the Abstracts of the Chemical Society.

In addition to issuing a complete edition of the "Chemical Abstracts," each nationality might also have partial editions, confined to the various classes, or to groups of classes—Physical, Inorganic, Organic, Analytical, Technological, Patents, &c., for the convenience of readers whose interests in the science are limited to certain branches only. This could be quite easily arranged by allotting the space devoted to any one section, in the general edition, always in multiples of sixteen pages, and paging each section separately; in some of the issues certain of the smaller sections would not be represented at all. At the end of the year, subscribers to the complete edition would have it properly collated in sections for binding. One general index would suffice and would be supplied with the partial editions as well as with the complete one. The issuing of partial editions would render it superfluous for the more specialised journals, &c., to continue the publication of separate extracts; they could either arrange for their subscription to include the appropriate partial edition issued as above, or leave the matter entirely in the hands of their subscribers themselves.

In addition to the all-round economy, and increased efficiency, which ought to result from concerted action on some such basis as that sketched above, there would be very considerable advantages of another kind. For example, anyone who desired to supply himself directly with a considerable proportion of the current literature would not find a large part of his library stored, as at present, with repeated abstracts of the same papers. Another great advantage would be the simplification of "References," which would result. Thus, suppose an author, of a date subsequent to the introduction of the system, wished to mention the work of some other author; he would require to give only one reference, not to the paper itself (unless he specially desired to give this as well), but to the international abstract, in some such way as the following:—C. A. 1910, IV., 123. This would mean: Chemical Abstracts, Volume published in 1910, Class IV. (say, General Organic Chemistry), Abstract No. 123 (not page 123). Any English, French, or German reader could then refer to his own edition and turn up the appropriate abstract without the least difficulty. There, in addition to the abstract itself, he would get any particulars as to the place, date, &c., of the original paper not given in the first reference.

As already indicated, these suggestions are put forward tentatively, and are not to be looked upon as embodying a complete scheme. Should the proposal meet with sufficient approval to lead to its being put into practice, very many points will require careful consideration and elaboration in order to ensure success.

A step in the direction of an international scheme has already been taken, but only for physico-chemical papers, and not on the general lines here recommended. The

actual initiation of that scheme shows, however, that the difficulties in the way of the other ought not to be insuperable.

Chemistry Department,
University of Edinburgh

SOME PHYSICAL CHARACTERS OF THE SODIUM BORATES, WITH A NEW AND RAPID METHOD FOR THE DETERMINATION OF MELTING-POINTS.*

By CHARLES HUTCHENS BURGESS AND ALFRED HOLLIMAN

SOME time ago we published a note containing some new observations on the solubility of metallic oxides in fused boric anhydride (*Journ. Chem. Soc. Proc.*, 1903, p. 221). Since its publication we have been further studying some of the points therein mentioned, but have been in part anticipated by W. Guertel (*Zeit. Anorg. Chem.*, vol. xl., [2], pp. 225 and 268; vol. xl., [3], p. 337), who has examined many of the phenomena we remarked, in a more complete manner. As, however, our experiments do not cover exactly the same ground as his, we have arranged in the following paper the results relating to the sodium borates, which we believe are completely new, and, at the same time, present many interesting features towards the study of these complex bodies.

When a quantity of ordinary pure borax glass is heated for some hours at a temperature which gives it about the consistency of a thick syrup, it gradually changes to a mass of colourless crystals. The crystallisation begins at two or three points on the surface of the mass, generally around a particle of dirt, or minute fragment of imperfectly fused borax, and spreads in more or less spherulitic growths throughout the glassy portion. As the crystals grow, there appears to be a contraction of volume, since the glass around them appears as raised hummocks, and a subsequent investigation of the specific gravities of the crystals and glass showed that this was really the case.

The crystals do not seem to grow at a uniform rate. They start rapidly, but as development continues, they take longer and longer to form, so that many hours are occupied in changing from pure glass to a holocrystalline aggregate.

We have not been able to isolate any individual crystals, and so study their characters, but the whole crystalline mass appears to be composed of dense matted clusters of very minute needles, which are doubly refracting, and have a pearly lustre. They are about as soluble in water as ordinary borax glass, are not hygroscopic, and melt at a higher temperature than the glass, into which they are reconverted on melting, and then cooling quickly.

We find, however, that it is not borax glass alone which exhibits this phenomenon of crystallisation on re-heating, but that the glasses obtained by fusing mixtures of boric anhydride and sodium carbonate, in which the ratio of the boric anhydride to the sodium carbonate is not 2 : 1, also exhibit it in varying degree.

Thus all mixtures in which the ratio varies from 6 : 1 to 8 : 5, give a glass when fused, and are all capable of being changed completely into crystals on re-heating, exactly like borax. Mixtures in which the boric anhydride is present in greater proportion than 6 : 1, only change with difficulty on prolonged heating, and when they do, the crystals are always found to be mixed with more or less truly glassy material, till, when the ratio 40 : 1 is reached, it seems impossible to obtain crystals at all. So far as we can ascertain, a mixture of this composition is always a true glass in any circumstances.

Mixtures, on the other hand, in which the ratio of boric anhydride is less than 8 : 5 when fused, and allowed to cool, yield nearly opaque, white substances, which seem to be

micro-crystalline. Nevertheless, these mixtures, if heated to a high temperature, and then suddenly chilled by being poured into mercury, also yield glasses.

The glasses obtained by this sudden chilling seem to be very unstable, as on gently heating by means of a Bunsen flame, they change completely, and almost instantaneously, into crystals.

There seems then to be a gradual alteration in the rapidity and completeness with which this change occurs, and as it seemed probable that the crystallisation of some borate rich in sodium was the cause of it, we proceeded to determine what was the composition of the borate richest in sodium which could be obtained by fusing boric anhydride with sodium carbonate.

When boric anhydride is fused with sodium carbonate, carbon dioxide is evolved, and the product may be regarded as boric anhydride combined with sodium oxide (Na_2O). Thus, by heating boric anhydride with a large excess of sodium carbonate, and determining the amount of carbonate decomposed, the greatest proportion in which boric anhydride combines with sodium oxide can be ascertained, and ought to give the composition of the richest sodium borate obtainable by fusion.

We have performed this experiment several times, and have obtained the following results:—

- i. One part of B_2O_3 combines with 1.29 parts Na_2O .
- ii. One " " " 1.34 "
- iii. One " " " 1.32 "

These results are probably a little too low, as the sodium carbonate loses some carbon dioxide merely on heating alone, but this amount is negligible, and does not in any way affect the conclusion that the product obtained in this way is not sodium metaborate (NaBO_2), in which the ratio of boric anhydride to sodium oxide is 1 : 1, and that sodium orthoborate ($\text{Na}_2\text{B}_2\text{O}_7$), in which the ratio is 1 : 3, cannot in any case be formed by fusion of boric anhydride and sodium carbonate.

The object of the research became thus threefold:—

a. To determine what compounds are present in crystals obtained with various mixtures of boric anhydride and sodium carbonate.

b. What is the nature of the glass.

c. What is the nature of the change from glass to crystals.

The most obvious method seemed to be to determine the melting points of crystals and glasses of varying composition, to see if compounds existed, and to compare and correlate the melting point curves obtained. To do this it was necessary to employ some new melting-point method, as none is known by which the melting-point of glasses can be determined at all accurately.

We devised an apparatus which is somewhat similar to the "meldometer" described by Joly (*Roy. Irish Acad.*, 1889), and we found it to be both rapid and peculiarly suitable in the case of plastic substances, which have hitherto been supposed to possess no definite melting-point.* Our apparatus is represented in Fig. 1.

A uniform piece of platinum-wire, A A, about 4 cm. long, was welded to two stouter pieces of the same metal, B B. These were sealed into two thin glass tubes, and were welded to two thick copper wires, C C, which conveyed the current. The whole was fixed by two rubber stoppers in a glass tube, with an opening at D.

A small bead of the material whose melting-point was desired, was made on one end of a very thin platinum-wire, to which a weight of about a gramme was attached.

A current of 4–6 amperes was passed through the wire A A so as to raise its temperature considerably above that at which the bead melted. The bead was then inserted through the opening D, when on touching the wire it became fused. The current was switched off, and the bead, on solidifying, remained attached to the edge of the wire A A. Air currents were prevented by closing the opening D with a test-tube.

* We use the words "melting-point" to denote the sudden decrease in viscosity which occurs at a very well defined temperature in glasses.

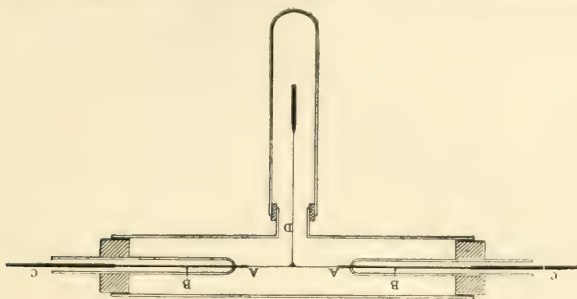


FIG. 1.

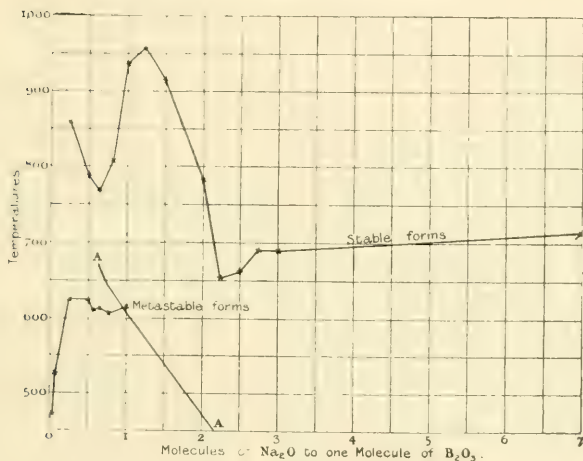


FIG. 2.

A slowly increasing current was then passed through the wire till the portion of the bead in contact with it melted, when the weight and bead fell into the test-tube. The moment this occurred, the voltage between the ends of the wire and the ampères passing through it were carefully noted. From the values obtained the resistance was calculated, and thence the temperature.

The weight hanging from the bead had no decided effect on the melting-point. We found that with weights varying from 0.2-5 grms., the bead dropped off at practically identical temperatures. This temperature at which beads of various compounds drop off the wire is extremely well defined, even in the case of substances which become plastic on heating, like glass, so that provided no chemical change occurs during the heating, the method proved rapid and elegant. A certain amount of heat is conducted away by the ends of the thick platinum-wires BB to which they the thinner one AA is welded, and also by the bead itself. It therefore became necessary to calibrate the wire by means of pure salts of known melting-points.

We found this was a matter of some difficulty, as very many of the most ordinary salts were found to decompose to some extent on heating. Sodium chloride, sodium carbonate, potassium iodide, calcium chloride, and strontium chloride all underwent change. Of these salts sodium chloride was very little attacked, but after only a few minutes' fusion we found it had absorbed quite an appreciable amount of oxygen, being converted into the peroxide. Potassium iodide changed in part to iodate, sodium carbonate to the peroxide, and calcium and strontium chlorides to the oxides.

These changes completely prevented any accurate melting-point determinations, so after repeated trials we adopted potassium nitrate, lithium chloride, and potassium chloride as standards. It is true that potassium nitrate decomposes on heating, but as the nitrite (to which it changes) has almost the same melting-point, the small amount of change was found to be immaterial. The chlorides we employed seemed to be, on the whole, very stable.

The melting-points given in Carnelley's tables for these

three standard substances were assumed as correct; they were used in fixing three points on the temperature-resistance curve.

Thus, any temperature between the melting-points of potassium nitrate and potassium chloride could be obtained by interpolation from the measured resistance, and those above the melting-point of potassium chloride by extrapolation. The results did not seem to contain an error larger than 1 per cent, so that we considered the method was satisfactory enough. The melting-point curves for the glasses and crystals are represented on Fig. 2. The curve for the glasses presents some features which are difficult to explain, since, so far as we are aware, no such curve has before been described.

The addition of sodium oxide to boric anhydride raises the melting-point continuously till a mixture of composition $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ is reached. There seems to be no depression of the melting-point at all, thereby differing from the case of ordinary solution, and indicating the probability that there is no solid phase.

The curve then remains fairly level till a composition $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ is reached, when it falls irregularly to $\frac{1}{3}\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$.

The last point we could obtain on this curve was with composition $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$, where the melting-point practically coincided with the temperature of change from the glassy to the crystalline state of this mixture. Indeed, it is a little above it, but it was possible by fairly rapid heating to melt the bead before the change had occurred.

At present we are unable to state exactly what the meaning of this melting-point curve for the glasses may be. Glasses have hitherto been supposed to possess no sharp melting-point, but this did not seem to be the case, as our results for each different temperature were remarkably close and well defined.

The melting-point curve for the crystals is more easily explainable than that of the glass.

We were unable to obtain any point on it between pure boric anhydride and a mixture of composition $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$. This was because the crystallisation of the small mass of substance in the beads we employed for the melting-point determinations took an extremely long time, and also because the devitrification was never complete except in the neighbourhood of the mixture $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$.

From a mixture of composition $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ the melting-point falls nearly uniformly till $5\text{Na}_2\text{O} \cdot 8\text{B}_2\text{O}_3$ is reached, at which point it begins to rise rapidly. The mixture $5\text{NaO} \cdot 8\text{B}_2\text{O}_3$ would then appear to be a marked eutectic-point.

The summit of the curve is reached with composition $5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$, when it falls again to a mixture which may be considered to have the composition $5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3 + 4\text{Na}_2\text{CO}_3$, and which represents the eutectic-point between $5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ and Na_2CO_3 .

The further addition of sodium carbonate causes a gentle, almost uniform rise in the melting-points.

As the summit occurs with composition $5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$, and as this very nearly agrees with the analysis of the borate richest in sodium, which can be obtained on fusion of boric anhydride and sodium carbonate, this would seem to indicate a compound.

The results of these melting-point determinations of the crystalline mixtures indicates that borax ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$) is not a definite compound in this state, but is almost a eutectic mixture of the borate with composition $5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ and one of composition $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$, for the existence of which we have other evidence.

This melting-point curve for the crystalline forms of these various mixtures cannot be regarded as truly representing either the *solidus* or *liquidus*. It seems probable that in this case they are situated close to each other, and that our melting-points really represent temperatures close to the liquidus. The fact that a mass of crystals would apparently melt almost completely at an almost constant temperature certainly indicates that there cannot be any

very great difference between the liquidus and solidus, and, as in the cases studied by Heycock and Neville, that the actually determined melting-points lie probably very near to the liquidus.

The following table gives the melting-points for the various glasses and crystals:—

Composition of mixture.	Melting-point	
	Glass.	Crystals.
B_2O_3	468°	—
$\text{Na}_2\text{O} \cdot 40\text{B}_2\text{O}_3$	470	—
$\text{Na}_2\text{O} \cdot 16\text{B}_2\text{O}_3$	528	—
$\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	628	858°
$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$	628	791
$9\text{Na}_2\text{O} \cdot 16\text{B}_2\text{O}_3$	613	—
$5\text{Na}_2\text{O} \cdot 8\text{B}_2\text{O}_3$	620	777
$3\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	610	815
$\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$	613	930
$5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	—	960
$5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3 + \text{Na}_2\text{CO}_3$	—	917
$5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3 + 3\text{Na}_2\text{CO}_3$	—	783
$5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3 + 4\text{Na}_2\text{CO}_3$	—	654
$5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3 + 5\text{Na}_2\text{CO}_3$	—	664
$5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3 + 6\text{Na}_2\text{CO}_3$	—	692
$5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3 + 7\text{Na}_2\text{CO}_3$	—	685
$5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3 + 27\text{Na}_2\text{CO}_3$	—	722

(To be continued).

A CHEAP KIPP'S APPARATUS.

By F. SOUTHERDEN, B.Sc., F.I.C.

IN many elementary experiments where a controllable stream of gas is required some inexpensive form of Kipp's apparatus becomes necessary. The writer has found the



contrivance here figured to be satisfactory. It may be fitted up in a few minutes, and is convenient to handle. Only a brief explanation need be given. An ordinary

"lime-tower" is the main feature, and down the centre of this passes a piece of wide-bore tubing, which fits loosely the constriction in the tower. This very effectually prevents solid entering the lower bulb, the zinc, marble, or iron sulphide being filled in after the tube is in position, whilst its open end is plugged with a stick or glass rod. The neck of the funnel is drawn out slightly, and a piece of glass tube attached so as to reach the bottom of the tower. To replenish the acid when exhausted it is blown up into the funnel, and emptied out. The piece of glass rod shown with the rubber cap serves as a stopper to the funnel when required, and to the outer tube when putting in fresh zinc; at other times it rests in the funnel.

Of course a tap-funnel and glass stopcock to the exit-tube makes a more elegant but needlessly expensive form of the apparatus. If used for sulphuretted hydrogen a clock-glass may be placed over the mouth of the funnel.

Royal Albert Memorial College, Lancaster.

AN YTTRIC EARTH NEAR TO GADOLINIUM.

By G. URBAIN

IN 1895, M. Lecoq de Boisbaudran (*Comptes Rendus*, cxxi.) observed in certain dysprosiferous terbias a feeble absorption band, $\lambda = 488$, which he considered to be characteristic of an unknown element. He denoted this unknown substance by Z δ . Demarcay made similar observations (*Comptes Rendus*, cxxxi.; *CHEMICAL NEWS*, lxxvii., 97).

For several years I have been working upon the yttric earths, attempting to separate the different terms of the series, and to reduce the intermediate fractions to a minimum. The first portions of the fractionation consist of pale rose europium oxide and white gadolinium oxide; these are followed by coloured earths, the fractions gradually darkening in colour. The darkest earths show the absorption spectrum of dysprosium to a marked degree. In the intermediate fractions, between gadolinium and dysprosium, I have obtained by three different methods coloured earths whose absorption spectra consist of the single band of Z δ ($\lambda = 488$).

METHOD I. Fractionation of Double Nitrates of the Earths and Nickel.—The object of this fractionation was to reduce to a minimum the intermediate fractions between gadolinium and the following earths. I will describe it in detail in a future paper. The heads gave white gadolinium oxide; the tails gave very dark oxides, whose olive coloured solutions gave a strongly marked spectrum of dysprosium (consisting of three bands in the blue and violet which resemble those of praseodymium in their breadth and general appearance) a feeble spectrum of holmium, and a diffuse and almost imperceptible band of Z δ .

The intermediate fractions consist of less highly coloured oxides, whose almost colourless solutions give the single absorption band of Z δ ($\lambda = 488$).

METHOD II. Fractionation of the Simple Nitrates in the presence of Bismuth Nitrate.—Of the simple nitrates of the rare earths containing 5 molecules of water, the nitrate of gadolinium is the least soluble (Demarcay, *Comptes Rendus*, cxxx.). I have found that the solubility of the isomorphous nitrate of bismuth is intermediate between those of the nitrates of gadolinium and samarium. On fractionation, therefore, bismuth nitrate should collect at two points of the series on either side of gadolinium, granted the minimum of solubility in case of the nitrate of the latter. I thus hoped to effect a new separation in the series, the method being similar to that already employed by M. Lacombe and myself in the separation of samarium and europium (*Comptes Rendus*, cxxvii. and cxxviii.).

400 series of crystallisations of twenty fractions, or about 8000 crystallisations, were necessary before a positive result was obtained.

The fractions between gadolinium and dysprosium, which I expected to be of pure bismuth nitrate, contained a small quantity of a dark earth. The absorption spectrum of this earth consists only of the band of Z δ . Therefore the nitrate of Z δ has the same solubility as the nitrate of bismuth.

METHOD III. Fractionation of the Ethyl Sulphates.—M. Lacombe and myself have gone much further in the fractionation of the ethyl sulphates of the earths of this group than we were able to do in 1898 (*Ann. de Chim. et de Phys.*, 1900, xix.), and in every case the absorption spectrum of the earths isolated from the fractions between gadolinium and dysprosium consisted only of the band of Z δ .

By these different methods I have been able to obtain nearly 100 grms. of these earths, which I have put together, and am fractionating at the present time.

In no case have I been able to obtain the results announced by R. Marc (*Ber.*, 1902, xxxv.). The band $\lambda = 464$ which he observed could not belong to the earths of this group, since their solutions when they contain dysprosium have a greenish and not a pink tint.

M. Lecoq de Boisbaudran only observed the band $\lambda = 488$ (Z δ) in earths having other absorption spectra at the same time; the existence of an element characterised by this feeble band could only be hypothetical. My results, however, show clearly the presence of a new element, which is quite distinct from dysprosium.

I have prepared a fair quantity of this new earth, and hope to determine whether it consists of one or more than one element.

It is indeed possible that the earths which I have obtained contain, besides the element characterised by the band $\lambda = 488$, another element without an absorption spectrum. The oxides are all brown, and are mixed with peroxides; but so far it is impossible to decide whether these properties belong to elements with absorption spectrum Z δ , and to dysprosium, or to a substance without an absorption spectrum which occurs with them, and to which should be given the name of terbium.

I have kept, provisionally, the notation Z δ for this element which possesses one single absorption band $\lambda = 488$.—*Comptes Rendus*, cxxxix., No. 19.

HYDRONITRIC ACID AND THE INORGANIC TRINITRIDES.*

By I. M. DENNIS and A. W. BROWNIE

Continued from p. 1741.

I. HISTORICAL (continued).

3. Properties and Reactions of Hydronitric Acid and the Inorganic Trinitrides.

THE properties of anhydrous hydronitric acid have been described by Curtius and Radenhausen (*Journ. Prakt. Chem.*, [2], xliii., 207). They have also described the action of a 7 per cent aqueous solution of the acid upon different metals (*Ber.*, xxxiii., 3023). It acts upon metallic iron, zinc, copper, aluminium, and magnesium with vigorous evolution of hydrogen, while a more concentrated solution appears to attack even gold and silver. Curtius and Risson found that in aqueous solution the acid is very slowly decomposed by boiling with moderately dilute mineral acids, but remains unchanged on boiling with pure water (*Journ. Prakt. Chem.*, [2], lviii., 261). During distillation practically all of the acid comes over with the first quarter of the liquid, leaving behind a very dilute solution, which distils unchanged. Aqueous solutions of the acid, even when very dilute, may be kept in stoppered glass bottles indefinitely without decomposition. In concentrated

* From the *Journal of the American Chemical Society*, xxi., No. 6.

aqueous solution it is, however, dangerously explosive (Curtius, *Ber.*, xxiii., 3023).

Ostwald determined by measuring the electrical conductivity of hydronitric acid that it was slightly stronger than acetic acid. His experimental data seem to be inaccessible. Two other investigators almost simultaneously repeated his work. Hantzsch found that the conductivity increased with the temperature (*Ber.*, xxxii., 3066), West measured the conductivity of the acid and of its sodium salt (*Journ. Chem. Soc.*, lxxvii., 705). He finds the strength of the acid at 25° to be slightly greater than that of acetic acid, and about one-seventieth that of hydrochloric acid.

In 1895, Peratoner and Oddo examined the gaseous products obtained by the decomposition of certain compounds of hydronitric acid in the hope of finding argon in case this should be polymeric nitrogen (*Gazz. Chim. Ital.*, xxv., II., 13; *Chem. Centrbl.*, xc., 2, 864). Only traces of argon were found, coming probably from the air dissolved in the solutions.

This subject was further studied by Szarvasy (*Journ. Chem.*, Soc., lxxvii., 603).

See also Peratoner and Oddo (*Gazz. Chim. Ital.*, xxx., II., 95; *Chem. Centrbl.*, 1900, II., 660).

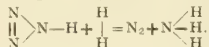
With regard to the structure of hydronitric acid, three lines of evidence tend to support the current belief that the compound contains a closed ring composed of three nitrogen atoms, and has the structural formula—



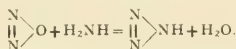
1. Fischer (*Liebig's Ann. Chem.*, xc., 67) showed that phenyltrinitride (diazobenzenimide) has the structure—



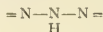
which had already been suggested by Kekulé (*Lehrbuch*, iii., 230). And from this, by the saponification with alcoholic potassium hydroxide of an appropriate substitution product (see reference to Nöling's work above), potassium trinitride is obtained. 2. Dennis and Doan (*Journ. Am. Chem. Soc.*, xviii., 970) found that the decomposition of thalous trinitride in a current of hydrogen yielded both ammonia and nitrogen, which may be expressed—



3. Erdmann suggests that the formation of hydronitric acid by the method of Wislicenus is proof of its structure (*Lehrbuch d. Anorg.*, 2te Auf., p. 190).



In opposition to the foregoing is the belief of Armstrong (*CHEMICAL NEWS*, lxxvii., 153), based upon a study of the optical properties of the acid, that it may be an unsaturated compound with the formula—



Mendeleeff ("Principles of Chemistry," 2nd Eng. ed., vol. i., p. 267) regards hydronitric acid as being theoretically derived from secondary ammonium orthonitrate, by the abstraction of 4 molecules of water, as follows:—



From the corresponding primary salt, nitrous oxide is considered to be derived, and ammonium trinitride from the tertiary salt by a similar theoretical process. It may not be out of place to mention here that orthonitric acid, predicted years ago by Mendeleeff, has recently been made by Erdmann (*Zeit. Anorg. Chem.*, xxxii., 431).

Berthelot and Matignon (*Comptes Rendus*, cxiii., 672),

and Bach (*Zeit. Phys. Chem.*, ix., 241) have almost simultaneously determined the thermochemical data for hydronitric acid.

Details concerning the explosive character of the salts of hydronitric acid will be found in the articles of Curtius, Dennis and Benedict, Dennis and Doan, and Berthelot and Vieille (*Ann. Chem. Phys.*, [7], ii., 339).

Hydronitric acid and its salts have a pronounced toxic effect upon living organisms. When the fumes of the acid are inhaled, even in very small amounts, they produce a characteristic headache and dizziness. The effect upon certain mammals of the subcutaneous injection of small doses of the sodium salt, is the production of spasms, and symptoms of heart and lung paralysis (Loew, *Ber.*, xxiv., 2947). In the case of bacterial life, growth is prevented (Schattenfroth, *Arch. für Hyg.*, xxvii., 231).

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, November 16th, 1901

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

PROFESSOR P. C. RAY was formally admitted a Fellow of the Society.

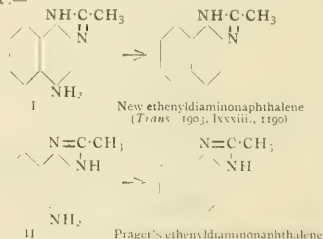
Certificates were read for the first time in favour of Messrs. William Frederick Arnaud, A.I.C., 17, Maddox Street, W.; George Douglas Clarkson, Ash House, Mirfield, Yorks.; Samuel George Eade, 10, Eagle Street, Port Talbot, S. Wales; Carl Richard Hennings, Ph.D., 19, St. Dunstan's Hill, E.C.; Tudor Foulkes Jones, B.Sc., Bro Dawel, Bangor, North Wales; William Sloan Mills, M.A., Queen's College, Galway; Harold Schreder, Lithgow, New South Wales; Ernest Wheeler, 335, Park Road, Oldham, Lancs.; John Henry Becher Wiggington, Kennington Cross, S.E.

A certificate in favour of the following was authorised by the Council for presentation for ballot under By-law 1:—Gustav Komppa, Ph.D., Polytechnic, Helsingfors.

Of the following papers, those marked * were read:—

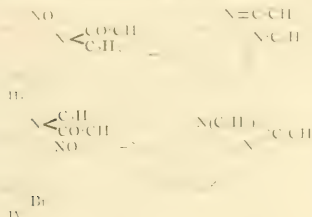
*189. "The Isomerism of the Amidines of the Naphthalene Series." (Fifth communication on Anhydro-bases). By RAPHAEL MELDOLA and JOSEPH HENRY LANE.

When 2:4-dinitro-aceto- α -naphthalide is reduced by tin and hydrochloric acid, the aminoamidine (M. and S. ethenylidiaminonaphthalene) has the α -NH constitution (No. I.), and the isomeric base (Markfeldt's), produced when iron and hydrochloric acid are used for reduction, has the β -NH constitution (No. II.). The constitution of the corresponding ethenylidiaminonaphthalenes follows from this result:—

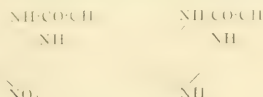


This conclusion has been reached by a comparison of the N-alkylamidines obtained by the direct alkylation of the

ethenylammonaphthalenes with the N-alkylamides prepared synthetically and of known constitution. Thus the N-ethylamide, prepared by the direct ethylation of Prager's base, is identical with the base prepared by reducing the compound No. III., and the isomeric N-ethylamide, obtained by the ethylation of the *meta*-ethenylammonaphthalene (cf. *Ann.* 1903, lxxxiii, 1403), is identical with the base prepared by reducing compound No. IV. and the *ortho*-bromonaphthalene product.

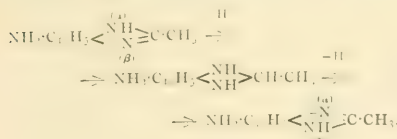


It has thus been shown that the isomerism of the ethenyltriaminonaphthalenes is a case of structural isomerism brought about by a novel and, up to the present time, unique method, namely, the action of different reducing agents on the same dinitro compound. In explanation of this isomerisation, the hypothesis is advanced that one of the reducing agents, probably the iron, effects a fractional reduction of the nitro-groups, while the other reducing agent attacks both nitro-groups simultaneously. The formation of the amidine ring would thus take place in one case under the orienting influence of the NO_2 -group, and in the other case under the orienting influence of the NH_2 -group, and the resulting anhydroses might under these conditions be expected to be isomeric, the intermediate phases being the compounds:—



The investigation is being extended to the benzene series, so as to obtain evidence, if possible, of the intermediate phases.

The transformation of the α -NH-aminoamidine into the β -NH-aminoamidine (*Trans.*, 1903, lxxxiii, 1200) is explained by the temporary saturation of the amidine ring by hydrogen and the subsequent removal of the element in accordance with the scheme—



DISCUSSION.

Dr. LANDER asked whether Professor Meldola had observed tautomeric relationships between the isomeric amidines. The work might be regarded as settling the nature of the so-called "virtual" tautomerism of the open-chain mixed amidines discovered by von Pechmann.

Dr. KOHN inquired whether the author had tried to reduce the dinitro-compound electrolytically. If not, this method might throw some light on the suggested hypothesis of the formation of the two amidines, since the stages observed in the electrolytic reduction of nitro-compounds

were somewhat different from those which obtained with the use of metals and acid.

Dr. DIVERS asked whether the production of one or other aminoamidine, according to the metal employed, might not rather be due to the reducing action of stannous or ferrous chloride than to that of the metal itself. But even although due to the action of the metal, there may be difference in the effect, because the reduction is not caused actually by hydrogen, but by the combined simultaneous action of the metal and the 2:4-dinitroaceto- α -naphthalide on the hydrochloric acid.

Dr. MORGAN remarked that the hypothesis that iron and hydrochloric acid reduced the nitro-groups of 2:4-dinitroaceto- α -naphthalide successively was supported by the known behaviour of this reducing agent towards *m*-dinitro-compounds in the benzene series. The production of *m*-nitraniline from *m*-dinitrobenzene by the action of limited amounts of iron and acid had formerly been patented (D.R.P. 67018). He had likewise found that, in the case of dinitrostyrene, the use of iron and water, with a small amount of acetic or hydrochloric acid as catalyst, led to the production of nitrosesidine, whereas complete reduction to diaminesidine was effected by employing tin and hydrochloric acid.

Quite recently, Meister, Lucius, and Brünig (D.R.P. 151768, *Abstr.*, 1904, i, 943) had obtained 1-acetylaminodiaminonaphthalene from 2:4-dinitroaceto- α -naphthalide by using iron and acetic acid. As the authors assumed that this acetyltriamine was an intermediate product in the formation of one of the two isomeric aminoamidines, it would be of interest to ascertain whether the acetylated base would yield by direct dehydration the isomeride predicted by their theory.

Professor MELDOLA, in reply, stated that both ferrous and stannous chlorides had been tried as reducing agents. The latter gave rise to the M. and S. base, the former was apparently without action under ordinary conditions. Several metals other than tin and iron had been used as reducing agents, and the results were described in the present and in former papers. Thus far, the action of iron in giving rise directly to Markfeldt's base appeared to be unique.

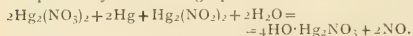
The practical difficulty that presented itself in all the experiments was the great insolubility of 2:4-dinitroaceto- α -naphthalide. This compound was practically insoluble in cold alcohol and acetic acid. With concentrated sulphuric acid as a solvent, there was a danger of the acetyl group being split off. For this reason, electrolytic reduction had not hitherto been attempted. He agreed with Dr. Lander's view that the results arrived at might be regarded as settling the question of the "virtual" tautomerism of the amidines raised by von Pechmann. There seemed to be no tautomeric relations between the isomeric amidines or aminoamidines. The patented process for preparing acetyltriaminonaphthalene referred to by Dr. Morgan had not yet been tried.

*190. "Theory of the Production of Mercurous Nitrite and of its Conversion into various Mercury Nitrates." By PRAFULLA CHANDRA RAY.

Mercurous nitrite is the sole product, other than water, of the immediate action of mercury on dilute nitric acid containing any nitrous acid. In the absence of the latter acid, the former is quite inactive. The formation of the salt may be expressed by the equation $2\text{Hg} + \text{NO} + \text{HNO}_2 \rightarrow \text{Hg}_2(\text{NO}_2)_2 + \text{H}_2\text{O}$, but it is in part converted by nitric acid into nitrate and nitrous acid. At suitable temperatures and in presence of the right proportions of water and nitric acid, a stage is soon reached in which the quantity of nitrite produced by nitrous acid is just balanced by that decomposed by nitric acid. There then ensues for some time a steady accumulation of mercurous nitrite, during which the production of permanent nitrite is due wholly to the nitric acid, as expressed by the equation $2\text{Hg} + 4\text{HNO}_3 \rightarrow \text{Hg}_2(\text{NO}_3)_2 + 2\text{H}_2\text{O}$. So long as this equation is valid, there is present in the

solution an unvarying quantity of nitrous acid, acting, as it were, catalytically. Analyses of portions of the solution drawn off close to the surface of the mercury give support to the foregoing theoretical considerations. When working at 35°, the mercurous nitrite and mercurous nitrate are present in molecular proportion.

The basic constitution of Marignac's mercurous nitrates is traced to the behaviour of mercuric nitrite, which is itself derived from mercurous nitrite (*Trans.*, 1904, lxxxv., 523). The production of hemi-hydroxy-mercurous nitrate is explained by the following equation:—



Two oxy-mercurous nitrates, one orange-yellow and the other lemon yellow, the latter best known through Gerhardt's work, the former a salt obtained by the author, are both traced to their origin from mercurous nitrite through the agency of mercuric nitrite. Direct oxidising action, whether by nitric acid or by air, is demonstrated to be at least unnecessary for the production of the mercuric and mercurous nitrates which result from the prolonged changes occurring in a nitric acid solution of mercury.

*191. "Amidechloroiodides." By GEORGE DRUCE LANDER and HARRY EDWIN LAWS.

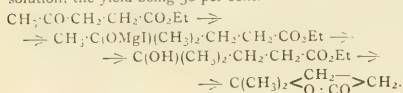
When pure dry hydrogen iodide is passed into a solution of benzanilide imidechloride in light petroleum, an amidechloroiodide, probably having the constitution $\text{Ph} \cdot \text{CCl} \cdot \text{NHPh}$, is precipitated as a microcrystalline yellow powder (m. p. 106° with decomposition). A similar result is obtained with the imide chloride of benzo- β -toluide.

With arylamines and sodium alkylloxides, amidines and iminoethers respectively are formed, the chloroiodides first losing hydriodic acid and the imidechlorides then reacting in the usual way. As the iodine atom is not capable of giving reactions of substitution, no direct evidence in support of the given constitution can be adduced, but the compounds are analogous in physical properties and chemical behaviour to Biltz's amideiodides, $\text{RCI}_2 \cdot \text{NH}_2$.

Benzamidedi-iodide, $\text{PhCl}_2 \cdot \text{NH}_2$, can be easily prepared by means of dry hydrogen iodide instead of the concentrated aqueous solution used by Biltz. Benzonitrile is formed from it by the action of alcoholic sodium ethoxide.

192. "A New Synthesis of isoCaprolactone and certain Derivatives." By DAVID TREVOR JONES and GEORGE TATTERSALL.

isoCaprolactone may be easily obtained by the action of magnesium methyl iodide on ethyl laevulate in ethereal solution, the yield being 30 per cent.



On treating isocaprolactone with phosphorus pentabromide in the cold and pouring the product into alcohol, ethyl γ -bromoisocaproate, $(\text{CH}_2)_3 \cdot \text{CBr} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, is formed, which decomposes on distillation.

Ethyl γ -methylallylacate, $\text{CH}_2 \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, obtained by treating ethyl γ -bromoisocaproate with diethyl aniline at 140° for ten minutes, is a fragrant mobile liquid boiling at 85° under 20 m.m. pressure.

γ -Methylallylacetic (γ -methyl- Δ^1 -pentenoic) acid, $\text{CH}_2 \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, produced when the preceding ester is hydrolysed with aqueous caustic soda, is a liquid with a pungent odour; it is volatile in steam and polymerises on distillation.

193. "The Influence of Substitution in the Nucleus on the Rate of Oxidation of the Side-Chain." Part II. Oxidation of the Halogen Derivatives of Toluene." By JULIUS BEREND COHEN and JAMES MILLER.

The authors have studied the behaviour of the isomeric chlorobromo- and dibromo-toluenes, and the following

table contains a synopsis of the results obtained with these substances, and also with the dichlorotoluenes (compare *Trans.*, 1904, lxxxv., 174), the compounds on the left being least, those on the right most, rapidly oxidised. The bracket indicates an approximately equal rate of oxidation.

Cl·Cl ..	3·5	2·5	2·6	2·3	2·4	3·4
Cl·Br ..	3·5	2·5	2·6	2·3	2·4	3·4
Br·Cl ..		2·5		2·3	2·4	3·4
Br·Br ..	3·5	2·3	2·5	2·6	2·4	3·4

The order of oxidation is the same in all three series with the exception of the 2:3-dibromotoluene, which follows the 3:5- instead of the 2:5- and 2:6-compounds, as in the other two series.

A comparison of the pairs of chlorobromo-compounds with reversed positions of the halogens indicates that the compound in which bromine occupies the meta-position is the less rapidly oxidised of the two.

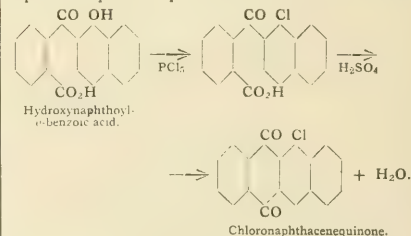
The dibromotoluenes are in all cases less rapidly oxidised than the dichlorotoluenes, and where bromine is in the meta-position the retarding action is much more pronounced than in the other cases.

The position occupied by the chlorobromotoluenes as regards the rate of oxidation is not always midway between the other two series (the dichloro- and dibromo-toluenes), but appears at first sight to be quite irregular; it may be accounted for by the fact that the three monobromotoluenes are much more rapidly oxidised than the three monochlorotoluenes, and if, as appears probable, two different halogens interfere less with each other's individual influence than two similar halogens, the apparent irregularities vanish. The problem is, however, thereby rendered more complex.

The authors propose to introduce the word "isotopic" (*isos*, equal; *τόπος*, place) to indicate similar compounds substituted in the same positions. Thus the 2:3-dichloro-, 2:3-chlorobromo-, 3:2-chlorobromo-, and 2:3-dibromo-toluenes would be "isotopic" substances.

194. "The Halogen Derivatives of Naphthacenequinone." By SAMUEL SHROWDER PICKLES and CHARLES WEIZMANN.

In the systematic investigation of the halogen derivatives of naphthacenequinone, $\text{C}_{18}\text{H}_{10}\text{O}_2$, the preparation of these compounds by direct bromination or chlorination is not advisable, inasmuch as the separation and identification of the products would be a matter of considerable difficulty. The authors have succeeded in obtaining a monochloro-derivative, in which the position of the chlorine atom is defined by first treating hydroxynaphthoyl-*o*-benzoic acid with phosphorus pentachloride, thus obtaining a chloronaphthoyl-*o*-benzoic acid. On treating this acid with concentrated sulphuric acid, water is eliminated and chloronaphthacenequinone is produced.



195. "The Constitution of Pyrazolidone Derivatives: β -Phenylazoisovaleric Acid and β -Phenylhydrazidobutyric Acid." By BERTRAM PRENTICE.

When 1-phenyl-3:3-dimethyl-5-pyrazolidone (m. p. 74–75°) is hydrolysed with barium hydroxide, β -phenylazois-

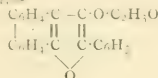
valeric acid (m. p. 57—58°) is produced (Ber., 1896, cxcvii., 272). When treated with reducing agents in acid solution, β -phenylazo-valeric acid yields 1-phenyl-3,3-dimethyl-5-pyrazolidone, which is formed by the condensation of the intermediate β -phenylhydrazido-valeric acid.

1-Phenyl-3-methyl-5-pyrazolidone, prepared according to Knorr and Duden's method (Ber., 1893, xxvi., 103) was also hydrolysed, and yielded 5-8-phenylhydrazidobutyric acid, $C_6H_5 \cdot NH \cdot NH \cdot CH(CH_3) \cdot CH_2 \cdot CO_2H$ (m. p. 96—97°), an unstable substance with strong reducing properties, which on fusion loses 1 molecule of water, and becomes converted into 1-phenyl-3-methyl-5-pyrazolidone (m. p. 81—85°).

196. "Preliminary Notice of some Condensations of Phenanthraquinone with Ketonic Compounds." By FRANCIS ROBERT JAPP and JAMES WOOD.

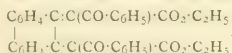
Very few condensations of this class have hitherto been studied, and in these only alkaline condensing agents have been employed; but in many cases such agents give no result. The authors find, however, that acetic anhydride containing a little sulphuric acid frequently brings about the desired reaction.

Thus a mixture of phenanthraquinone and acetophenone yields, with this reagent—slowly at the ordinary temperature, more rapidly at 40°—3-acetoxy-2-phenyl-4:5-diphenyl-1,4-dioxane.



which crystallises from benzene in slender needles (m. p. 232°).

When phenanthraquinone and ethyl benzoylacetate, on the other hand, ethyl diphenylenedibenzoylmalonate (ethyl β , β' -diphenylene- α , α' -dibenzoylbutadiene- α , α' -dicarboxylate),—



is obtained, the acetic anhydride in this case furnishing no part of the resultant molecule. This substance crystallises from benzene in rectangular plates with bevelled edges. It softens and almost melts between 170° and 174°, but immediately re-solidifies, finally melting sharply at 223°. This phenomenon is due to the transformation of the condensation compound into an isomeride, which crystallises from acetic acid in slender needles melting at 223.5°.

Under the foregoing conditions, phenanthraquinone also yields condensation products with ethyl acetacetate, ethyl malonate, and analogous compounds.

The authors wish to reserve the study of these various condensations.

197. "The Decomposition of Ethylene Iodide under the Influence of the Iodide Ion." By ARTHUR SLATOR.

The following is a summary of the results obtained:—

1. Ethylene iodide in aqueous-alcoholic solution decomposes quantitatively in the presence of potassium iodide, yielding ethylene and iodine.

2. The velocity of reaction is proportional to the concentration of ethylene iodide, and also to that of the iodide ion, showing that the potassium iodide takes some direct (or catalytic) part in the reaction. The temperature quotient for 10° is 2.5.

3. This reaction is distinct from that between ethylene iodide and sodium thiosulphate, for the two reactions may be superimposed without any great mutual interference.

4. The rate of liberation of iodine from solutions of methyl iodide, isopropyl iodide, and ethyl iodoacetate is accelerated by the addition of potassium iodide.

5. Ethylene bromide in presence of potassium iodide liberates iodine according to the equation, $C_2H_4IBr + KI = C_2H_4I_2 + KBr$.

6. The reaction velocity is proportional to the concentration of the bromide and also to that of the potassium iodide, and the temperature quotient for 10° is 2.45.

Ethylene iodide is probably not an intermediate product in the reaction. The iodide decomposes about three times as fast as the bromide.

198. "The Spectrum Green's Attributed to Chlorophyll, and its Relation to the Spectrum of Living Green Tissues." By WALTER NOEL HARTLEY.

The author formerly showed (Trans., 1891, lix., 106) that the alcoholic extract of fresh green leaves and also the alcoholic extract of dried leaves do not give the same absorption spectrum as the material in the living leaf when examined under normal conditions. This difference was believed to be due either to the formation or the occurrence of acid in the extract and in the dried leaves, this acid effecting chemical changes in the colouring matter. The same changes in the spectrum could be brought about in the living leaf in an oxidising atmosphere under the action of intense sunlight, and these are conditions which would lead to the formation of an acid.

Marchlewski and Schunck (Trans., 1900, lxxvii., 1080) cast doubt on the accuracy of the author's observations, and more particularly on the efficiency of the process described for extracting the bluish-green colouring matter. Sorby's "blue chlorophyll," in an unchanged condition from an alcoholic extract of green leaves. The author therefore found it desirable to have the process re-examined by an independent observer, and subsequently he repeated the experiments himself. Further measurements of spectra are recorded which confirm the accuracy of the original observations.

199. "Studies on Comparative Cryoscopy. Part II. The Aromatic Acids in Phenol Solution." By PHILIP WILFRED ROBERTSON.

As in the case of the fatty acids, an intimate relationship is shown between the association and the velocity of esterification; those acids which are most difficult to esterify associate the least.

Substitution in the ortho-position with respect to the carboxyl group reduces the "rate" of association. The substituent groups or atoms may be arranged in the following order:—OH, CH₃, Cl, Br, NO₂. The lighter groups exert only a slight influence, but there is a marked diminution in the case of the heavier groups.

In the case of acids containing two ortho-substituents, however, there is practically no association, whether the substituent is heavy or light. Compounds of this nature are characterised by the fact that they yield esters only with the greatest difficulty, whereas the velocity of esterification of the ortho-substituted benzoic acids is dependent on the weight of the substituting group or atom.

Substitution of the nitro-group in the meta-position still causes a reduction in the "rate" of association, but a lighter group, like methyl, has no influence in this position.

The hydroxylic and dibasic acids are characterised by their sparing solubility in phenol.

200. Isomeric Change of Diacylanilides into Acylaminoketones. Transformation of Dibenzoylaminobenzophenone into 1-Benzoylaminobenzophenone. By FREDERICK DANIEL CHATTAWAY and WILLIAM HENRY LEWIS.

It has recently been shown (Trans., 1904, lxxxv., 386, 499) that diacyl derivatives of aromatic amines can undergo an intramolecular re-arrangement whereby an acyl group leaves the nitrogen and enters the nucleus in an ortho- or a para-position with respect to this element. The transformation of such diacylaminobenzophenone derivatives can progress beyond the first stage, so that two groups may enter the ring in positions probably ortho- and para- to the nitrogen. The isolation of 1-amino-2:4-dibenzoylbenzene from the

product obtained by heating aniline (1 mol.) with benzoyl chloride (3 mols.) were described.

Erratum.—P. 275, col. 2, line 30 from top, after "permanganate" insert "in the presence of potassium persulphate."

THE FARADAY SOCIETY.

Wednesday, November 23rd, 1904.

Mr. W. R. COOPER, in the Chair.

THE Ninth Ordinary Meeting was held at the Institution of Electrical Engineers.

The minutes of the previous meeting were duly confirmed.

THE CHAIRMAN moved that the hearty congratulations of the Society be tendered to the President, Sir Joseph Wilson Swan, on the occasion of the recent dignity which had been conferred upon him by the King. The motion was carried unanimously amid applause.

Professor L. KAHLBERG, Ph.D., presented a paper on "*Recent Investigations bearing on the Theory of Electrolytic Dissociation*," which, in the absence of the author, was read in abstract by the Secretary.

In creating the theory of electrolytic dissociation the phenomena of actual electrolysis have played a minor part. It has rather been based on the observation that for many aqueous solutions the molecular conductivity increases with the dilution, and that the osmotic pressure, lowering of freezing-point, and similar physical constants are abnormally great. The hypothesis is thus virtually connected with van 't Hoff's theory of dilute solutions which it generalises in the form $PV = iRT$, where i , the so-called degree of dissociation, is unity for non-electrolytes, and greater than one for electrolytes. The author is of opinion that the theory is supported by isolated facts only.

Comparisons of the molecular conductivities with the freezing-points at 0° and boiling-points at 95° were made by the author in 1901, with typical solutions of electrolytes and non-electrolytes, and no such connection between those quantities as demanded by the theory was found.

According to the theory, molecular conductivities should increase with the volume, but in practice that is often not the case.

According to the Nernst-Thomson rule, dissociation is caused by the high specific inductive capacity of the solvent, but cases are cited, such as liquid hydrocyanic acid, where a higher dielectric constant than water has accompanied by lower conducting—and therefore ionising—power.

Additive properties are not a valid argument in favour of the theory, because they occur in quantities such as molecular heats and molecular refractions, where ionisation is out of the question.

The colours of solutions have been attributed to the free ions present, but copper, nickel, and cobalt oleates are insulators, and yet bear the characteristic colours of the supposed metallic ions.

Instantaneous reactions sometimes occur between insulating solutions, and hence cannot be regarded as taking place between the free ions present.

A strong argument against the hypothesis is that it cannot be harmonised with the law of mass-action. The agreements obtained by Ostwald in his application of the dilution law to solutions of weak organic acids are only very rough, and to electrolytes *par excellence* it cannot be applied at all. Rudolphi's and van 't Hoff's amended formulae are purely empirical.

The power of coagulating colloids has been ascribed to free ions, but such power is not confined to solutions of electrolytes.

It is in the realm of non-aqueous solutions that the theory proves especially important. We now know of such solutions that conduct electricity even better than aqueous

solutions, and yet yield higher molecular weights than those computed from the formulae of the solutes. The researches of Walden on liquid sulphur dioxide are quoted as being particularly conclusive.

The theory has been applied to fused salts. The author questions the validity of such application to what are practically 100 per cent solutions; the hypothesis is avowedly only strictly true for infinitely dilute solutions.

Professor Kahlenberg does not think the hypothesis can be retained even in a modified form. It must give way to a conception which takes into account the affinity—of the same nature as chemical affinity—between solvent and solute. "*The processes of solution and chemical action are identical in character, and chemical compounds are merely the cleavage pieces of solutions placed under special stress or duress represented by the so-called purifying processes.*" Thus chemical action is merely a special case of solution, and the process of solution is the general case of the interaction of bodies resulting from their specific attractions for one another. A dilute solution is merely a limiting case. The abnormal values of molecular weights of substances in solution as determined by change of vapour tension, freezing- or melting-points, is merely a measure of the affinity between solute and solvent, and has nothing to do with any supposed dissociation; the calculation of molecular conductivities is founded upon the erroneous supposition that the solvent plays no part in the conduction. Recent determinations of osmotic pressures by the author have similarly shown that these depend on the nature of both membrane and liquids, and are by no means in accordance with the requirements of the gas laws. Here, again, as in solutions, *affinity* is the determining quantity.

Mr. W. C. D. WHETHAM, in a written communication, pointed out that the problem of the nature of solution was independent of the difference between electrolytes and non-electrolytes, which was all the theory attempted to explain. The ions must be conceived as being free from each other, not from all chemical combination, in order to explain the observed phenomena of conduction.

Professor ABEGG also sent in a written communication. Professor Kahlenberg's reasons for doubting the theory are merely facts which cannot be explained by the Arrhenius theory alone. The latter explains the behaviour of dilute aqueous solutions, where the non-ionised molecules are, as a rule, not associated, and not cases where association occurs, such as in non-aqueous solutions. The author further overlooks the fact that conductivity depends on the mobility of the ions, as well as on the degree of ionisation. The theory can be harmonised with the law of mass action, as the work of Rothmund and Drucker and Jahn has shown.

Dr. G. RUDORF referred to the question of the colour of solutions, and showed that on the assumption that the molecule of copper sulphate has nearly the same light-absorbing properties as the ion, all difficulties disappear. The theory quite explains the reactions mentioned in benzene solution, if only very few ions are assumed to be present.

Dr. T. M. LOWRY said that Prof. Kahlenberg's criticisms were mostly expended on a theory which was not the dissociation hypothesis as conceived to-day. The theory does hold good for concentrated solutions, only we are not yet able to measure the degree of ionisation in such cases. The gas laws are not quite true for moderately dilute solutions, because some of the molecules of the solutes are in combination, and not free. He dealt at length with the various points raised by the author.

Dr. H. BORN showed that Prof. Kahlenberg's capital mistake was that he attacked everything that had ever been said or done with the theory. He ignored recent modifications of it that the ideas of hydrolysis, complex ions, and association have caused.

Dr. H. SAND (communicated) dealt with the differences between the theory of Clausius and that of Arrhenius, and discussed some of the approximate assumptions that lead

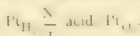
to numerical disagreements in the applications of the latter.

Dr. C. H. DESCH discussed Prof. Kahlenberg's experiments with copper oleate in benzene solution, and described some experiments of his own bearing on the subject. He thought the difficulties raised by non-aqueous solutions very serious ones.

Mr. F. S. SMITHS drew attention to the theory of Traube, which gave numerical expression to some of the conceptions of solution apparently held by Prof. Kahlenberg, and explained the Arrhenius coefficient i in terms of the affinity between solute and solvent.

Mr. F. J. BRISLEE, M.Sc., communicated a paper entitled "The Potential of the Hydrogen Electrode," which was read by Dr. P. M. PERKIN.

Measurements of the potential of the combination



show different results when the oxygen electrode is charged with oxygen electrolytically, or charged by passing oxygen gas through the liquid. Experiments were made to determine the influence of hydrogen peroxide, ozone, and persulphuric acid upon the oxygen potential. The results obtained showed that the addition of hydrogen peroxide lowered the oxygen potential, while addition of ozone and potassium persulphate raised it.

By employing platinum electrodes of extreme thinness (prepared by depositing platinum on glass), the same potential of the combination was obtained independently of the method employed for charging the electrodes. This potential showed a good agreement with that calculated from the Helmholtz formula.

Mr. H. L. JOLY, referring to the effect of persulphates, said that in accumulators it had been proved that their presence did not account for the rise of E.M.F. on charge.

by the action of potash, which converts this acid and its derivatives into crotonic compounds.

Oxidation of Acetol.—André Kling.—The author describes the action of various classes of oxidising agents upon acetol, and discusses the results of his experiments.

The Formation of Formic Aldehyde in the Combustion of Tobacco.—A. Trillat.—Already noticed.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution before Easter:—

A Christmas Course of Lectures (experimentally illustrated and adapted to a juvenile auditory) on "Ancient and Modern Methods of Measuring Time," by Mr. Henry Cunynghame.

Professor L. C. Miall, Fullerian Professor of Physiology, R.I., six lectures on "Adaptation and History in the Structure and Life of Animals."

Professor Karl Pearson, three lectures on "Some Recent Biometric Studies."

Professor W. E. Dalby, two lectures on "Engineering."

Mr. A. H. Savage Landor, two lectures on "Exploration in the Philippines."

Mr. Churton Collins, two lectures on (I.) "The Religion of Shakespeare." (II.) "The Philosophy and Significance of 'The Tempest.'"

Professor W. Schlich, two lectures on "Forestry in the British Empire."

Mr. J. H. Teall, two lectures on "Recent Work of the Geological Survey."

Professor H. H. Turner, three lectures on "Recent Astronomical Progress."

Professor R. Meldola two lectures on "Synthetic Chemistry" (Experimental).

Sir Alexander Mackenzie, three lectures on the "Bohemian School of Music" (with Musical Illustrations).

Mr. D. G. Hogarth, two lectures on "Archæology."

Professor J. J. Thomson, three lectures on "Electrical Properties of Radio-active Substances."

The Right Hon. Lord Rayleigh, three lectures on "Some Controversial Questions of Optics."

The Friday Evening Meetings will begin on January 20, when a Discourse will be delivered by Professor Sir James Dewar on "New Low Temperature Phenomena." Succeding Discourses will probably be given by Dr. E. A. Wilson, Mr. Cecil Smith, Mr. J. W. Gordon, Professor H. Marshall Ward, Chevalier G. Marconi, Professor J. J. Thomson, Sir Squire Bancroft, Professor G. H. Bryan, Professor J. Wright, Professor T. C. Allbut, the Right Hon. Lord Rayleigh, and other gentlemen.

Separation and Isolation of Reducing Sugars by means of Hydrazine.—Emil Votocek and R. Vondracek.

—By the reaction of sugar hydrazones with aromatic hydrazines the reducing sugars can be identified, *i.e.*, such sugars can be precipitated systematically from mixtures by application of suitably chosen hydrazines. By preliminary experiments (colour reactions, distillation with hydrochloric acid, &c.), it is first determined which series of sugars the syrup to be analysed contains, *e.g.*, whether hexose and pentose, hexose and methylpentose, pentose and methylpentose, &c., are present. Then the total sugar is determined by Fehlings' solution, and the syrup diluted with water till it contains 5 per cent of sugar. The equivalent weight of a suitable hydrazine or its acetate is then added to the diluted solution, the hydrazine thus formed is removed, and another aromatic hydrazine added direct to the mother-liquor to convert the second sugar into hydrazine (or osazone). The hydrazine is then identified by its melting-point. This process can be repeated for a third sugar. *Ber.*, xxxviii., No. 15.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise stated.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. CXXXIX., No. 19, November 7, 1904.

The Effect of Low Temperatures upon Dyes.

—Jules Schmidlen.—The temperature of liquid air does not affect dyes when in the solid state, nor when fixed upon silk or woollen material. The colour of alcoholic solutions of some dyes is weakened at the above temperatures; this is particularly noticeable with the rosanilines, in whose solutions a beautiful green fluorescence becomes visible as the colour disappears. Probably at ordinary temperatures the fluorescence is masked by the colour.

Heat of Combustion of Triphenylmethyl and of some Derivatives of Triphenylmethane.—Jules Schmidlen.—The results of a number of experiments are given.

Preparation of Aurous Iodide by the Action of Iodine on Gold.—Fernand Meyer.—Already noticed.

β -Bromobutyric Acid.—M. Lespieau.—The amide of β -bromobutyric acid was obtained by saturating allyl cyanide with hydrobromic acid gas in the cold. When this amide was saponified by warm hydrobromic acid, an acid was obtained which melted at 17 – 18° and boiled at 122° under 16 m.m. pressure. The formula by analysis is $\text{C}_4\text{H}_7\text{BrO}_2$; melting-point by cryoscopic methods 166° . The melting- and boiling-points of this acid and its derivatives differ from those of the α - and γ -acids, therefore the bromine must be in the β -position. This is further proved

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Colonel C. W. Carr-Calthrop, Mr. Cecil Hanbury, Dr. E. Graham Little, Mr. Hugh Makins, and Mr. E. Reinach were elected Members.

MEETINGS FOR THE WEEK.

MONDAY, 12th.—Society of Dyers and Colourists, 8. "Bleaching Agents, and the Methods of Application," by F. W. Walker. "Application of Sulphide Colours in the Dyeing of Chrome Leather," by Dr. W. Epstein.

WEDNESDAY, 14th.—Chemical, 5.30. "Hydrolyses of Ammonium Salts," by V. H. Veley. "Viscosity of Liquid Mixtures" (Part II.), by A. E. Dunstan.

"The Diazo-reaction in the Diphenyl Series—Part II., Ethoxybenzidine," by J. C. Cain. "The Sulphate and the Phosphate of the Dimercurammonium Series," by F. C. Ray. "Method for the Direct Production of certain Aminoazo-compounds," by R. Meldola and L. Eynon.

Society of Arts, 8. "The Patent Laws," by Chas. D. Abel.

RECTIFIED SPIRIT

(SPIRITS OF WINE.)

B.P. and higher strengths. Duty paid; or
Duty Free under Finance Act 1902.

METHYLATED SPIRIT

Special Quotations to large
Institutions.

BOORD & SON,

DISTILLERS SINCE 1750,

115-121 Tooley Street,
LONDON, S.E.

OLD PLATINUM

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver
Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and Purchased.



ACETONE,

Chemically and Tech. pure.

METHYL-SPIRIT.

WOOD

NAPHTHA.

METHYLENE, Type Regie.

ACETON OIL.

&c.

PLATINUM

UTENSILS, SCRAP,
LAMP-ENDS, &c.,

Purchased at highest prices by—
DERBY & CO., LTD., 44, CLERKENWELL ROAD LONDON.
N.B.—Platinum Sold.

MR. EDWARD ARNOLD'S NEW BOOKS.

THE CHEMICAL SYNTHESIS OF VITAL PRODUCTS

AND THE

INTER-RELATIONS BETWEEN ORGANIC COMPOUNDS

BY

R. MELDOLA, F.R.S., V.P.C.S., F.I.C., &c.,
Professor of Chemistry in the City and Guilds of London
Technical College, Finsbury.

Super Royal 8vo. 21s. net.

THE BECQUEREL RAYS AND THE PROPERTIES OF RADIUM.

By the Hon. R. J. STRUTT,
Fellow of Trinity College, Cambridge.

Demy 8vo. With Diagrams. 8s. 6d. net.

AN INTRODUCTION TO

THE THEORY OF OPTICS.

By ARTHUR SCHUSTER, Ph.D., Sc.D., F.R.S.,
Professor of Physics at the University of Manchester.

Demy 8vo. With numerous Diagrams. 15s. net.

THE ELECTRIC FURNACE.

By HENRI MOISSAN,

Professor of Chemistry at the Sorbonne.

Translated by A. T. de MOUILPIED, M.Sc., Ph.D.

Demy 8vo. With numerous Illustrations. 10s. 6d. net.

London: EDWARD ARNOLD, 41 & 43, Maddox St., W.

MELTING & BOILING-POINT TABLES.

BY

THOMAS CARNELLEY,

D.Sc. (Lond.), B.Sc. (Vict.), F.C.S.,

Professor of Chemistry in University College, Dundee.

The Standard and only work upon the subject.

2 Vols. Ry. 4to. 799 pp. 42s.

HARRISON & SONS, Pall Mall, London, S.W.

BRYAN CORCORAN LIM.

MILLSTONE BUILDERS,

WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.

Sole Makers of MILBURN'S

Patent Conoidal Stone Grinding Mills.
Especially suitable for certain materials, Wet or Dry.

Works and Warehouses: Back Church Lane.
Parcel Dept.: Basement of the Corn Exchange.
31, MARK LANE, LONDON.



CHEMICALS, Pure and Commercial.

For Scientific and Technical Purposes

Specialities: ETHERS, OHLOROFORM.

POLGLASE & CO., Type Vale Chemical Works, Skinnerburn-nd.
NEWCASTLE-ON-TYNE.

MICA

F. WIGGINS & SONS, 10, Tower Hill, E., & London.
102 & 103, Minorics, E.C.,

MICA MERCHANTS.

Manufacturers of Mica Goods or Electrical and ALL purposes.
Contractors to His Majesty's Government.

Chemische Fabrik Eidelstedt,

Joh. Oswaldowski, Altona E.

THE CHEMICAL NEWS.

VOL. XC., No. 2351.

RESEARCHES UPON THE CANON DIABLO METEORITE.

By HENRI MOISSAN.

A CERTAIN amount of work has been done upon the native iron found in Arizona, near the Canon Diablo. Koenig, then Mallard in 1892, noticed small fragments in it, which were hard enough to scratch corundum. In the same year Friedel, after having dissolved a small portion of the iron in hydrochloric acid, pointed out that it contained black diamonds. Finally, in 1893, we showed that certain fragments of this native iron, or meteorite, contained transparent diamonds.

Our first research was made upon a very small fragment of Canon Diablo iron, weighing only 4 grms.; it contained, however, one unmistakable point of extreme hardness, upon which a steel grindstone had no effect. We have since had the opportunity of continuing our work upon a much larger specimen weighing 183 k.grms., which was kindly placed at our disposal by M. Wallerant, Professor at the Sorbonne.

The rough irregular surface of this well-known meteorite is of a dark brown colour, and has a shivelled appearance. It contains those characteristic external cavities which, according to Daubrée, would be produced by the escape of a gas at high pressure.

The first process was to cut up the block of iron in order to examine the interior. This was done by M. Paul Regnard by means of a long steel ribbon saw. The meteorite was put in a carriage which could be moved forward slowly, while the ribbon saw was moved by four pulleys driven by steam. Under these conditions the saw penetrated easily enough to a depth of several centimetres within the block; but then the blade seemed to meet some very hard body, and no further headway was made. After some time it became necessary to change the saw and to make the carriage move more quickly. The work was continued for several hours without much result. Then suddenly the resisting object seemed to break, or else the blade passed round the obstacle, and was able again to move forwards. The sawing then began again regularly, but soon stopped as before, and in this way no fewer than twenty days were occupied in cutting this specimen of Canon Diablo iron into two parts. The sawed surface measured about 626 square c.m.; the left side seemed to be homogeneous, and was the colour and lustre of iron; on the right side there were five large marks of elliptical shape and three small ones.

These spots were of a grey or black colour. The major axis of the ellipse in the case of one measured 2.3 c.m., and the minor axis 2 c.m. Another had a major axis of 3.4 c.m. and a minor axis of 2.1 c.m. The little spots were practically circles of 1 c.m. diameter. Some of these spots were joined by broken irregular lines, or by fissures filled with a black material. The three largest spots were dark in colour, the others were grey. Certain of these spots were surrounded by a black material which formed a pad between the metal and the ellipse.

It was clear that it was these spots which had offered such a strong resistance to the saw, because round each of them the surface of the metal was not plane, but was furrowed, showing that the saw had met an obstacle and had moved out of the vertical to get round it.

By comparing this section of the block with specimens of the same origin in New York Museum, we have satisfied ourselves that this is the general aspect of the interior of

Canon Diablo iron. Also, by the kindness of Dr. Harvey, of the New York Natural History Museum, we have been able to compare it with sections of other meteorites, such as the Toluca meteorite, and we have found that they all present the same appearance.

When examined by the microscope the metallic surface seemed to be homogeneous, and the elliptical spots clear and crystalline.

The fissures joining the spots were filled with a black substance which had apparently been compressed. In the envelope of several of the ellipses masses of brilliant metallic crystals were found, but at other places, both round the ellipses and in the fissures, there were black masses of very finely grained structure. To analyse the meteorite chemically 53 k.grms. were dissolved in pure hydrochloric acid. It was immediately evident, as we have already shown, that the iron was not homogeneous, for it was attacked very irregularly by the acid. Where the sawed surface had been plane, raised striae quickly appeared, forming a system of slightly undulating parallel lines, cut, from place to place, by similar perpendicular lines.

But the following fact seemed the most interesting to us:—The ellipses turned out to be the sections of nodules, which quickly disaggregated in the hydrochloric acid and fell to the bottom of the vessel, leaving cavities with sharp edges, resembling those found on the outer surface of Canon Diablo iron and other meteorites.

The hydrogen set free during this reaction contained hydrocarbons, sulphuretted hydrogen, and phosphoretted hydrogen.

The analysis was divided into three parts:—(1) Analysis of the metal; (2) of the nodules; (3) of the carbon.

1. Analysis of the Metal.

We found the metal to be an alloy of iron and nickel containing small quantities of phosphorus, silicon, sulphur, and magnesium; there were also traces of cobalt, which have not hitherto been noticed. Thus the metallic part of Canon Diablo iron is far from being homogeneous. Certain fragments taken from the exterior contained iron and nickel in the following proportions for 100 parts of the mineral:—Iron, 95.64; nickel, 1.66. Iron, 95.26; nickel, 2.56. Iron, 94.03; nickel, 3.61. Iron, 96.31; nickel, 1.83. A specimen of density 7.703 from the inside of the meteorite gave the following figures on analysis:—

Iron	95.370
Nickel	3.945
Phosphorus	0.144
Substances insoluble in boiling HCl	0.260
Silicon	traces
Sulphur	traces
Carbon	not determined

This specimen clearly contained carbon, and being taken from near a nodule it was fairly rich in phosphorus. Specimens taken from parts at some distance from the nodules were found to be much poorer in phosphorus and carbon.

2. Analysis of the Nodules.

The nodule was separated from the block by means of a chisel and hammer.

In this nodule there were both metallic and black amorphous fragments. No weight was lost by heating it in a little tube to 700° C. When attacked by hydrochloric acid a large amount of sulphuretted hydrogen was set free. In the acid solution we found a large amount of iron, some nickel, and a very small quantity of cobalt, which was recognised by the borax bead test, and by the formation of a double nitrite of cobalt and nickel. The solution also contained phosphorus, silicon, calcium, and magnesium in small quantities. The insoluble portion contained silica, amorphous carbon, graphite, and black and transparent diamonds. The following figures were given by the quantitative analysis of a nodule:—

Iron	66.95	67.51
Nickel	1.93	1.77
Cobalt	traces	
Sulphur	22.15	19.91
Phosphorus	2.37	2.30
Silicon	small quantity	
Magnesium	traces	
Carbon	1.96	

Analysis of the Residue Insoluble in Hydrochloric Acid.

—The following was an analysis of the residue remaining after the 53 k.grms. previously mentioned had been treated with hydrochloric acid. After the treatment with acid, a residue remained in the bottom which, when dried, weighed about 800 grms. It consisted of a coarse powder containing brilliant needles and cubes. We separated these by use of a forceps.

	Needles.			Cubes.
	1.	2.	3.	
Phosphorus	26.97	25.95	25.95	26.46
Iron	71.63	72.15	73.51	72.43
Nickel	traces			
Carbon	traces			

There was no doubt about the presence of carbon, for after treatment with aqua regia a light insoluble deposit remained, which burnt in oxygen with the formation of carbon dioxide.

The crystals apparently consist of a phosphide of iron of formula P_2Fe_3 , and which theoretically would contain 26.95 per cent of phosphorus and 73.05 per cent of iron. The variations in the analyses of this crystallised phosphide are explained by Mr. Stead's work, in which he showed that phosphides obtained from steels containing phosphorus vary in composition.

This crystallised compound is fairly abundant, both in the striae of the nickel and iron alloy and in the neighbourhood of the nodules.

Presence of Carbon Silicide.—In the residue which remained after treatment with concentrated hydrofluoric acid and boiling sulphuric acid we found the characteristic green hexagonal crystals of carbon silicide. This is the first time that carbon silicide has been met with in nature, although it was obtained accidentally by M. Lebeau when he was preparing nickel silicides by the electric furnace.

3. Study of the Carbon.

The carbon, which is found in small and variable quantity in the alloy of nickel and iron far from the nodules, is partially converted into hydrocarbons when the metal is treated with hydrochloric acid, so that the black residue that remains only contains a portion of the total amount of carbon present in the Canon Diablo iron. The residue which remained after the iron had been attacked by acid weighed about 800 grms., and analysis showed that it contained 5.04 per cent of carbon.

This carbon was present in several different forms. Some of the fragments found in the residue were about $\frac{1}{4}$ of a c.c. in size, and were of a very irregular shape. The following varieties were met with:—

1. A light impalpable powder of a variable brown colour, which resulted from the decomposition of the carbon compounds contained in the iron nickel alloy.

2. Carbon occurring in jagged slender fragments of a light colour, and which seemed to have been agglomerated by pressure.

3. Graphite, which was recognised by transforming it into graphitic oxide. This graphite is very rarely crystallised, but is almost always amorphous, and yields a dark brown graphitic oxide.

4. Smooth black diamonds. These were abundant in the residue, but were always very small.

5. Transparent diamonds in the form of octahedrons with rounded edges.

Sawdust of the Meteorite.—All the above qualitative work was verified by an analysis of the sawdust which

contained both the metal and the nodules. In it we found iron phosphide, carbon silicide, and the three varieties of carbon.

In conclusion, Canon Diablo iron contains the three forms of carbon—amorphous, graphitic, and crystalline. The latter consists both of black and transparent diamonds. But the interesting result of this work is that the diamonds are found to be surrounded by a sheath of carbon, and that they occur round the nodules of the Canon Diablo iron, nodules which contain silicon phosphorus, and above all sulphur.

To explain the formation of these nodules in the midst of the mass of iron we must have recourse to the interesting experiments of Mr. Stead. He has shown that if carburetted iron is kept at about 700° C. the iron carbide makes its way through the mass and collects in nuclei. This takes place just below and very near 700° C., and if the cooling is very slow, the process is quite complete. Also, according to Mr. Stead, phosphorus furnishes the same phenomenon, and if both are present the carbide collects round the phosphorus, as was the case in the nodules.

On the other hand, MM. Le Chatelier and Ziegler have shown that iron sulphide possesses the curious property of passing with great ease through the intercrystalline fissures, whatever be their nature, which occur in a mass of iron. The Canon Diablo meteorite certainly contains many fissures, and it is in these fissures, filled with carbon, that the diamonds are found. Thus it seems as though at a later period the sulphur had reacted upon the carbide and phosphide. Finally, we must add that if sulphur, phosphorus, and silicon tend to displace carbon from iron, the addition of nickel to iron also diminishes the solubility of carbon in the alloy. These two phenomena have combined to separate out the carbon from what must have been a liquid solution when carbon silicide was formed.

Later we propose to study the influence of pressure on these various reactions.—*Comptes Rendus*, November 14, CXXXIX., No. 20.

SOME PHYSICAL CHARACTERS OF THE SODIUM BORATES, WITH A NEW AND RAPID METHOD FOR THE DETERMINATION OF MELTING-POINTS.*

By CHARLES HUTCHENS BURGESS and ALFRED HOLT, jun.

(Concluded from p. 286).

WE have analysed a number of the glasses and crystals obtained with various mixtures, and obtained most unexpected and interesting results.

The analysis of a borate is always a matter of difficulty, but we found the following method worked quite well and gave accurate results:—A weighed quantity of the substance (glass or crystals in very fine powder) was evaporated to dryness twice with fairly strong hydrochloric acid. By this means all the sodium was converted into the chloride. The dry powder thus obtained was repeatedly treated with small quantities of ethyl alcohol, and evaporated to dryness. By this means all traces of hydrochloric acid were removed, as well as the whole of the boric acid, so that pure sodium chloride remained. This was dissolved in water and estimated by titration with N/10 silver nitrate solution, using potassium chromate as indicator.

The complete separation of the crystals from the glass was by no means an easy matter. We found that quite the easiest and most satisfactory method was to crush up the substance into coarse powder, and then to pick out with forceps the really glassy fragments and the crystalline masses. This was quite easy by using a lens.

* A Paper communicated to the Royal Society, October 27, 1904.

Though the crystals and glass have different specific gravities, it was not found possible to obtain a real separation by means of a heavy liquid. This was because pieces of material which looked wholly crystalline often contained glass in the interior, so that they would float anywhere in the liquid.

We also tried extraction with hot methyl alcohol, which is a solvent for boric anhydride, for if the crystals had been due to a separation of a borate from its solution in boric anhydride, this should have left the compound pure. As a matter of fact, we found that the methyl alcohol decomposed both the crystals and glass, giving methyl borate, boric acid, and sodium methylate. Both glass and crystals were decomposed at the same rate.

Attempts to use water as a means of separation were also failures, since the solubility of both glass and crystals is about the same.

The results of our analyses are as follows:—

(i.). *Mixture of Composition about $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$.*—This mixture crystallised completely in a few hours, giving a hard white completely crystalline mass. When about two-thirds had crystallised the glass and crystals were separated, and gave on analysis:—

Glass = 30.9 per cent Na_2O ; crystals = 31.0 per cent Na_2O .

(ii.). *Mixture of Composition about $3\text{Na}_2\text{O} \cdot 8\text{B}_2\text{O}_3$.*—This crystallised completely, and had the same characters as (i.). On analysis obtained:—

Glass = 25.86 per cent Na_2O ; crystals = 25.81 per cent Na_2O .

(iii.). *Mixture of Composition about $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$.*—This crystallised completely, and had the same characters as (i.). On analysis obtained:—

Glass = 18.70 per cent Na_2O ; crystals = 18.67 per cent Na_2O .

(iv.). *Mixture of Composition about $\text{Na}_2\text{O} \cdot 6\text{B}_2\text{O}_3$.*—This crystallised very nearly completely, but seemed to contain small translucent glass-like fragments. On analysis obtained:—

Glass = 11.5 per cent Na_2O ; crystals = 13.7 per cent Na_2O .

(v.). *Mixture of Composition about $\text{Na}_2\text{O} \cdot 8\text{B}_2\text{O}_3$.*—This did not crystallise completely. After very prolonged heating it nearly all changed to a crystalline mass with an almost waxy lustre, but which was not really wholly crystalline. There was always, in addition, a portion of the mass which remained a glass. On analysis obtained:—

Glass = 10.06 per cent Na_2O ; crystals = 11.90 per cent Na_2O .

(vi.). *Mixture of Composition about $\text{Na}_2\text{O} \cdot 12\text{B}_2\text{O}_3$.*—Only about half would crystallise, and this took a very long time. On analysis obtained:—

Glass = 2.1 per cent Na_2O ; crystals = 12.2 per cent Na_2O .

(vii.). *Mixture of Composition about $\text{Na}_2\text{O} \cdot 16\text{B}_2\text{O}_3$.*—After heating this mixture for several days only a very small amount crystallised. On analysis obtained:—

Glass = 4.18 per cent Na_2O ; crystals = 10.02 per cent Na_2O .

(viii.). *Mixture of Composition about $\text{Na}_2\text{O} \cdot 40\text{B}_2\text{O}_3$.*—This could not be crystallised at all.

From these numbers it appears that, with mixtures between $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, the crystals and glass have absolutely identical composition, but with mixtures containing more boric anhydride than $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ only a part (decreasing in quantity as the amount of boric anhydride present increases) crystallises, and this part has approximately the composition $\text{Na}_2\text{O} \cdot 6\text{B}_2\text{O}_3$.

As the crystals of the mixture of this composition contain more sodium than the glass, it seems probable that, could

one obtain the crystals really pure and not entangling any glass, the composition might approach that of $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$.

The nearness in composition of the crystals obtained from mixtures varying from $\text{Na}_2\text{O} \cdot 16\text{B}_2\text{O}_3$ to $\text{Na}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, makes it seem fairly certain that it is the same compound which separates out in all of them, and that the differences in the analyses are due to the crystals being mixed with more or less glass which it was impossible to remove. In experiment (vi.) the crystals and glass were particularly well separated, and the result is shown by the great difference in their analyses.

It seemed so curious that, with mixtures of composition $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ to $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$, the glass and crystals should give similar analytical results, that we thought it worth while to try fractional crystallisation of the glasses to see if we could detect any differences between the different crystalline portions.

The analyses of these various portions gave the following results:—

(i.). *For a Mixture of Composition about $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$.*

		Per cent Na_2O
First portion	Glass	29.7
	Crystals	29.3
Second portion	Glass	29.9
	Crystals	29.2
Third portion	Glass	30.3
	Crystals	30.5
Fourth portion	Glass	30.2
	Crystals	30.1

(ii.). *For a Mixture of Composition about $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$.*

		Per cent Na_2O
First portion	Glass	18.7
	Crystals	18.6
Second portion	Glass	18.6
	Crystals	18.4

We also fractionally crystallised borax itself five times, when the final crystalline portion was found to contain 30.8 per cent Na_2O , theory for $\text{Na}_2\text{B}_4\text{O}_7$ requiring 30.7 per cent Na_2O .

These differences are negligible, and the crystals that separate out from the glass have exactly the same composition from the beginning.

These results show at once that this crystallisation is not due to the separation of any single compound, as we had previously supposed, but that it is more probably due to the formation of mixed crystals or a solid solution from a supersaturated liquid.

All the various crystalline fractions obtained from any one glass of composition $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ to $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ were found to melt at identical temperatures, as also did the residual glasses. Further, the crystalline portions, when melted, gave glasses which had a melting-point identical with that of the previous residual glass, and these residual glasses could, in their turn, be changed to crystals with similar melting-points to those which had originally been separated.

This shows most conclusively the identity of the crystals and glass in chemical composition. We have also determined in the case of several mixtures the temperatures at which this crystallisation takes place. The curve indicating these temperatures is shown in Fig. 2 by the line joining A A.

A bead of the glass was put on the platinum wire of our melting-point apparatus, and the temperature raised extremely slowly, whilst the bead was watched with a lens. In the case of those mixtures which melted before the change occurred, no weight was attached to the bead. The crystallisation appeared to start at a fairly well defined temperature, and, if it was maintained, would gradually spread through the bead.

It is a little hard to say exactly what is the meaning of this curve A A (Fig. 2), and all that seems certain is that it

gives approximately the temperatures at which the rate of crystallisation assumes a sufficient velocity to visibly change the state of the substance.

From a consideration of the melting-point curves, together with the analytical and other observations we have described, it is possible to form some idea as to the nature of these glasses and the crystals into which they are wholly or partially transformable.

The glass must be regarded as a superfused—and, therefore, meta-stable—form of the crystals, behaving in several respects as if it were a liquid of enormous viscosity.

Now, on considering the behaviour of the glasses ranging in composition from pure boric anhydride to $\text{Na}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, it will be noticed that the supposition of the existence of a borate of about the composition $\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3$, which is dissolved in boric anhydride, will explain the observed facts. A mixture of composition $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ cannot be crystallised at all, and one of composition $\text{Na}_2\text{O} \cdot 16\text{B}_2\text{O}_3$ only partially crystallises; hence some point between these mixtures will give the maximum solubility of this borate in boric anhydride. On further increasing the amount of this borate present, the glass becomes a supersaturated and superfused liquid, the amount of crystallisation measuring the supersaturation.

Somewhere between $\text{Na}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ no free boric anhydride remains in the solution, and the whole mass will crystallise for the first time.

On further addition of sodium, another borate of composition near $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ begins to be formed, and we have shown that in any mixture between these two compounds both crystals and glass have identical compositions. We are here probably dealing with a case of solid solution, and the glass is merely its superfused form.

The character of the curve would indicate that there are two types of crystals: one rich in B_2O_3 , the other rich in Na_2O , and the lowest point of the curve is the eutectic-point formed by mixtures of these two.

That the crest of the curve does not occur with the composition $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ can be most conveniently explained by the fact that solid solutions cannot be treated as pure substances, and so a slight shifting of the maximum point is to be expected. The further depression of the melting-point curve probably indicates the eutectic-point between these crystals, rich in Na_2O , and sodium carbonate.

In conclusion, we wish to express our thanks to Professor H. B. Dixon and Mr. D. L. Chapman for the kindly interest they have taken in our work.

NOTE.—In the woodcuts illustrating this article (p. 285) Fig. 1 was accidentally inserted upside down.

(a) The Preparation of Sodium Amide.

Sodium amide was discovered about the year 1808 by Gay-Lussac and Thenard during an investigation of the properties and reactions of the then newly discovered metals, potassium and sodium ("Recherches Physico-chimiques," i., 337). Fifty years later it was subjected to further scrutiny by Beilstein and Geuther (*Liebigs Ann. Chem.*, 1858, cviii., 88). In 1892, W. Wislicenus first used it as a source of hydronitric acid, as stated above (*Ber.*, 1892, xxv., 2084). And finally, in 1894, Titherley prepared it in large quantities, and carefully studied its composition and many of its properties (*Journ. Chem. Soc.*, 1894, lxx., 504; lxxi., 460).

In the work here to be described, attention has been paid to the following considerations involved in the preparation of the compound:—(1) The action of molten sodium upon vessels of different materials; (2) construction of safe and convenient apparatus for enclosing the vessel containing the molten sodium; (3) necessary precautions to be employed in obtaining ammonia and sodium of sufficient purity; (4) means of securing good contact between the reacting substances; (5) the influence of temperature upon the nature of the product; and (6) method of analysing the product. These points will be considered in detail.

(1) The durability of vessels of different materials was tested in the course of several preliminary experiments, in which were used a porcelain boat, a platinum boat, a tube of hard, thick glass, a silver crucible and a nickel crucible. In each case several grms. of sodium were heated in the vessel under examination to a temperature of from 250° to 300°, in a current of ammonia, for about four hours. It was found that the interior of the porcelain boat had completely lost its glaze, and had assumed a dark brown colour, presumably due to the presence of free silicon liberated by the action of the sodium. The action upon the platinum boat was so marked that the amide obtained left, on treatment with water, a soft, spongy mass of platinum which retained the shape of the original product, and showed, under the microscope, a peculiar foliated structure. The glass tube stood the test surprisingly well. The surface, where it had come into direct contact with the molten sodium, was clouded to some extent, but the walls had not been eaten away appreciably. The silver crucible was acted upon to such an extent that the product firmly adhered to it on solidification, and showed a residue of numerous little spangles of silver when treated with water. When the sodium amide was prepared in a nickel crucible, however, the metal suffered no appreciable injury. The amide, after it had cooled, was easily removable by tapping the crucible and gently pressing its sides.

These results are not entirely in accord with those obtained by Titherley, who concluded that "platinum is only slowly corroded, but after a few weeks' constant use the metal becomes friable and much corroded" (*Journ. Chem. Soc.*, 1894, lxx., 504). In his later experiments he used a silver boat, saying that "the amide is practically without action on the metal." For preparing the amide on a large scale he suggests the use of a polished iron retort. This material, however, is open to serious objection. In the early experiments in this laboratory, dating back as far as 1895, a polished iron crucible was used in the preparation of the sodium amide, and the amide was then heated in a current of nitrous oxide in a second iron crucible to convert it into the trinitride. On dissolving the product of the second reaction in water and acidifying the solution with sulphuric acid, a heavy blue precipitate resulted. This was found to be essentially Prussian blue. On distilling off the hydronitric acid from this acidified solution the distillate was found to contain hydrocyanic acid as well. It was at first suspected that the carbon necessary to the formation of this hydrocyanic acid came from the kerosene in which the metallic sodium had been kept. To avoid the presence of this element, large pieces of sodium 9 inches long by 3 inches in diameter were procured, and after fully half an inch of the end had been cut off a core of sodium,

HYDRONITRIC ACID AND THE INORGANIC TRINITRIDES.*

By L. M. DENNIS and A. W. BROWNE.

(Continued from p. 288).

II.—EXPERIMENTAL.

A.—A Study of the Wislicenus' Method for Preparing Hydronitric Acid.

The hydronitric acid used in this investigation, as well as in the earlier ones carried on in this laboratory, has been made entirely by the Wislicenus method, and several years ago a careful examination of this process was begun with a view to ascertaining the conditions most favourable to a high percentage yield, especially when the sodium amide and sodium trinitride were prepared on a somewhat large scale. In describing our results, it may be well to classify the experiments under—(a) The Preparation of Sodium Amide; (b) The Preparation of Sodium Trinitride from Sodium Amide; and (c) The Preparation of Hydronitric Acid from Sodium Trinitride.

* From the *Journal of the American Chemical Society*, xxvi., No. 6, 1 *Ber.*, 1892, xxv., 2084.

not over 1.5 inches in diameter, was cut from the middle of the stick. The use of this material in the preparation of fresh samples of sodium amide in iron crucibles diminished the amounts of hydrocyanic acid and cyanides that were formed, but did not lead to the total avoidance of these products. It was then suspected that the carbide of iron present in the iron of the crucible might be attacked by the molten sodium and furnish the cyanogen. To test this supposition, fresh portions of the amide were prepared in crucibles made of nickel that was free from carbon, and no indication of the formation of either Prussian blue or hydrocyanic acid was obtained upon examination of the products. This formation of hydrocyanic acid, when iron vessels were used, has been pointed out by Szarvasy (*Journ. Chem. Soc.*, 1900, lxxvii., 603), who did not attempt to avoid the formation of cyanides, but separated the sodium cyanide from the sodium trinitride by treating the mixture with alcohol, the sodium cyanide remaining in solution. In all of the later work in this laboratory the sodium amide and the sodium trinitride have been prepared in nickel dishes 5 inches in diameter with perpendicular sides 3 inches high. As a result of long-continued use these dishes show signs of being somewhat attacked by the sodium, but the polishing of the dish with fine sea-sand before each run prevents any perceptible action upon it during the course of a single experiment.

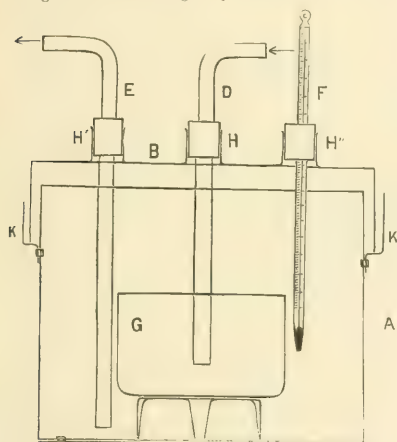


FIG. 1.

(2) In the above examination of the action of sodium on the material of the container the porcelain and platinum boats were heated in combustion tubing, the small silver and nickel crucibles in vertical glass tubes 2.5 inches in diameter and sealed at one end, while the large crucibles were heated in a perpendicular iron tube 3.5 inches in diameter and closed at each end with a heavy screw cap, the upper cap being perforated for the entrance and exit of the gases. For preparing the sodium amide in large amounts in the 5-inch nickel dishes above mentioned a special container was necessary, and after many experiments with different devices the apparatus shown in Fig. 1 was finally adopted.

The can A is of sheet iron and is provided with a double bottom and with a grooved top, κ, κ' , into which fits the cover B. This has three tubular openings, H, H', for rubber stoppers holding respectively the inlet tube for ammonia D, the outlet tube E, and the thermometer F. The nickel dish G stands upon a little tripod which

prevents direct contact between the dish and the highly heated bottom. No solder was used in making the can. All joints were fastened with rivets. After the cover has been placed in the grooved top, the outside annular space is tightly packed with asbestos and sand. The can is placed upon a thick iron plate, and heated with a triple burner.

(3) The ammonia used in several of the earlier experiments was prepared from ammonium chloride purified according to the method of Stas (*Untersuchungen über die Gesetze der chemischen Proportionen*, German translation by Aronstein, p. 49). A saturated solution of the ordinary "C. P." salt was boiled with one-tenth its volume of concentrated nitric acid until chlorine was no longer evolved. The crystals that separated on cooling were re-dissolved, and similarly evaporated with a smaller amount of acid. The crystals thus obtained were dried and mixed with twice their weight of calcium hydroxide. The mixture was then placed in a seamless copper bottle, was moistened with a little water, and was heated. By this means freedom from pyridine bases was insured. Comparative tests, however, in which other conditions were kept constant showed this extreme precaution to be unnecessary, and consequently ordinary "C. P." ammonium chloride was commonly employed. The ammonia was dried by passing it through a long chain of tubes containing fused sodium hydroxide and soda-lime. It was not found necessary to use a tube containing metallic sodium, as suggested by Titherley.

The sodium used in the experiments was cut from the centre of large sticks of the metal for the reason already mentioned. In handling the sodium, care was taken to warm all apparatus with which it was to be brought into contact, in order to drive off the film of moisture that is present at ordinary temperatures.

(4) To test the effect of greatly increasing the surface of contact between the reacting substances, two simultaneous experiments were conducted at the same temperature (about 250°). In one the ammonia was allowed to pass, as usual, over the surface of the molten sodium, while in the other it was led beneath the surface of the molten sodium through a hard glass tube. The results of the analysis of the products obtained by these two different treatments are given in Table I.

TABLE I.

Time of action Hours.	Per cent nitrogen.		Per cent sodium.	
	Found.	Theory.	Found.	Theory.
Surface contact only $4\frac{1}{2}$	31.0		61.2	
		35.9		59.0
Ammonia bubbling through the molten sodium 1	35.3		59.4	

These results show that when the ammonia passes through the molten sodium rather than over its surface, the formation of the amide is much accelerated—one hour's treatment by the bubbling process yielding a product of greater purity than four and one-half hour's treatment by surface contact. At the beginning of the experiment, after the sodium has become molten, the tube is submerged until it almost reaches the bottom of the dish. Then, from time to time, as the action proceeds, the tube is slightly raised, to avoid unnecessarily stirring up the amide, which sinks to the bottom as it is formed. Finally, when only a small globule of the metal remains, the tube is raised out of the liquid during the remainder of the treatment. No very perceptible error seems to be introduced by the slight action of the sodium upon the hard glass tube through which the ammonia is led. A tube of pure nickel, however, would undoubtedly be preferable to one of glass.

(5) The rapidity of action of the ammonia upon the molten sodium was found to increase with the temperature, as was to be expected. But at temperatures much above

350° (which was the temperature found on the whole to give the best practical results) there seemed to be some loss of the product by sublimation. This was noted also by Titherley, who worked chiefly between temperatures of 300° and 400°. At temperatures below 250°, on the other hand, rather curious results were obtained in our work. Although in every case the reaction seemed to have been completed, analysis invariably showed too low a percentage of nitrogen, and too high a percentage of sodium. Moreover, the deficit of nitrogen and excess of sodium showed a tendency to increase as the temperature became lower. At first this was attributed to the possible presence of uncombined sodium dissolved in the amide; but when pieces of the product were thrown upon water beneath an inverted glass tube filled with water, no hydrogen was liberated.

In Table II. are given the results of three experiments conducted at different temperatures in the neighbourhood of the temperature limit below which apparently a good product cannot be obtained. In the second and third of these experiments, about 100 grms. of sodium were employed in each case, while in the first a somewhat smaller amount was used. The method of bubbling was used in each case, and the reaction was allowed to proceed to completion.

TABLE II.

Per cent of—	Theory for NaNH ₂ .	No. 1. (250°)	No. 2. (240°)	No. 3. (200°)
Sodium	59.0	59.4	61.4	71.2
Nitrogen	35.9	35.3	33.6	23.4

It would appear from the foregoing results that at a temperature below 250° a satisfactory product is not obtained.

(6) Method of analysing the amide. Beilstein and Geuther (*Liebigs Ann. Chem.*, 1858, cviii., 88) made analyses of the compound by dissolving weighed samples in dilute hydrochloric acid in a long-necked flask, evaporating the solution to dryness, and determining the ratio between the amounts of sodium chloride and ammonium chloride formed.

Titherley (*Journ. Chem. Soc.*, 1894, lxxv., 504) in one series of experiments attempted to determine the yield of sodium amide by ascertaining the ratio between the weight of sodium taken and that of the product formed. In his second series he obtained the ratio between the increase in weight due to the change of sodium into amide and the weight of hydrogen evolved. In his experiments very satisfactory results were obtained by the use of this method, because, no doubt, of the extreme precautions he had taken to exclude air and moisture from the apparatus. For general use, however, the method used in his first series, at least, is open to the objection that it would fail to show even a considerable error due to the action of air or moisture upon the sodium, for the reason that the molecular weights of NaNH₂, NaO (= $\frac{1}{2}$ Na₂O₂) and NaOH are nearly the same.

It is evident that definite information concerning the yield of sodium amide can be obtained only by determining the percentages of both nitrogen and sodium in the product. To accomplish this a weighed portion of the product was placed in a Kjeldahl flask provided with a Reitmeier bulb and a dropping funnel. Water was introduced through the dropping funnel, and the ammonia set free by the decomposition of the sodium amide was distilled off into standard hydrochloric acid, the excess of acid being then determined by titrating back with standard sodium hydroxide, using methyl orange as the indicator. To ensure complete removal of the ammonia, the solution in the Kjeldahl flask was carefully evaporated to dryness, re-dissolved in fresh water and again evaporated to dryness. The percentage of sodium was determined by titrating the residue of sodium hydroxide in the flask with standard hydrochloric acid. This method was used in obtaining the results given in Tables I. and II.

(To be continued).

THE NOBEL PRIZES.

THE Nobel Prize for Physics has been awarded to Lord Rayleigh, Professor of Natural Philosophy at the Royal Institution. The Chemistry Prize is conferred upon Sir William Ramsay, Professor of Chemistry at University College.

The distribution of the Nobel Prizes took place in the Great Hall of the Academy of Music at Stockholm on the 10th inst., in the presence of King Oscar. Lord Rayleigh and Professor Ramsay received their Prizes, together with Diplomas and Gold Medals, in person from his Majesty. The sum of money attaching to each Prize amounts to 140,858 kroner (about £7825).

Lord Rayleigh proposes to present to Cambridge University the value of the Nobel Prize for Physics which has just been awarded to him.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, December 1st, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. A. D. COWPER and E. S. SIMPSON were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Andrea Angel, M.A., 41, Wellington Square, Oxford; James H. Campbell, 3, Morrison Terrace, North Road, Bellshill, N.B.; Bernard Collett, 79, Eastbourne Terrace, Gainsborough; Herbert Goodier, 16, Hall Road, Shipley; George Moss Lloyd, M.A., M.Sc., Queen's Road, Rock Ferry; Thomas Pennycuik, B.Sc., 6, Lorne Street, Fairfield, Liverpool; Bert Perrott, Ael-y-Bryn, Penywn Road, Neath, Glam.; William Henry Ratcliffe, B.Sc., 18, Wheeler Street, Maidstone; Frederick George Richards, 21, Dutton Street, Manchester; Harold Rudolph Rogers, B.A., 75, South Side, Clapham Common, S.W.

The PRESIDENT drew attention to the stand for the display of certificates of candidates for election which had been placed in the Library, and stated that, as the certificates are now printed in full in the *Proceedings*, they would not in future be brought down from the Library on the occasion of the ballot.

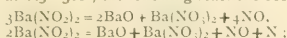
A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—William Harold Richard Allen; Walter Henry Bentley, B.A.; John Wycliff Black; Thomas Story Busher, B.A.; Lawrence Caldecott; Robert John Caldwell, B.Sc.; Peter Skinner Clark, M.B., Ch.M.; Frederick Clarkson-Harold; Jabez Horace Cooper, B.A.; William Crabb, B.Sc.; James Edward Cunningham; William Herbert Dalton; Harold Deane, B.Sc.; Francis Dickinson; Edward Evans; John Evans; Thomas Wallace Fagan, B.A.; John Kerr Forrest; Archie Willoughby Henszell; Thomas Reginald Hodgson; George William Thomas Horrod; John Kenneth Harold Inglis, M.A., B.Sc.; Thomas Campbell James, B.A., B.Sc.; Walter Richmond James; John Richard Johnson; Horace Francis Jones; William App Jones, Ph.D., A.M.; Alfred Francis Joseph; Gustav Komppa, Ph.D.; James Stanley Lauder; Arthur Garfield Levy, B.Sc.; James Patrick Longstaff, B.Sc.; Arthur Thomas McDougall, B.A.; Harold Joseph Clarke Mathews; Ernest Westby Millar; George Frederick Phillips, B.Sc.; Marie Jean Louis Ernest Rouillard, B.Sc.; Percy Edwin Spielmann; Harry Stanley, B.Sc.; Thomas Sutcliffe; Paul John Thibault; Arnold Bertram Tonkin; Douglas Frank Twiss, M.Sc.; Edwin Roy Watson, B.A., B.Sc.; Herbert Wood Watson, B.Sc.; Henry Bridges Weeks; William Henry Willcox, M.D., B.Sc.; Frank John Wyeth, M.A.

Of the following papers, those marked * were read :—

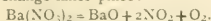
*201. "The Nitrides of the Alkali Metals and Metals of the Alkaline Earths and their Decomposition by Heat." By PRAFULLA CHANDRA RAY.

Solutions of the nitrides of barium and calcium, like those of the alkali metals, can be safely evaporated to dryness at the boiling temperature without decomposition or oxidation taking place.

A solution of magnesium nitride prepared by the double decomposition between barium nitride and magnesium sulphate is perfectly stable at the ordinary temperature, but it cannot be concentrated on the water-bath, as it undergoes decomposition even at 60°, evolving nitric oxide. The solution, when concentrated under reduced pressure over sulphuric acid, yields the hydrated salt $Mg(NO_2)_2 \cdot 3H_2O$, which, when kept in a desiccator, loses only one molecule of water, the dehydration not going any further. All the nitrides described have a faint yellow colour. When barium nitride is heated under reduced pressure at 225–300°, the following reactions occur :—



whereas at temperatures between 300° and 500° or upwards the following change takes place :—



The other nitrides behave similarly. In the earlier stages, the gaseous products of decomposition are mainly nitric oxide and nitrogen, in the second they are chiefly nitrogen peroxide and oxygen. It is difficult to distinguish sharply between these two stages, and an intermediate phase has been observed, $Ba(NO_2)_2 = Ba(NO_3)_2 + O_2$. The decomposition of magnesium nitride begins at 60°, and at 120° that of the first stage is complete, resulting in the formation of a basic nitrate, $Mg(NO_3)_2 \cdot MgO$, which is stable even at 175°.

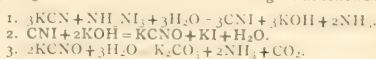
*202. "The Metallic Derivatives of Nitrogen Iodide and their Bearing on its Constitution." By OSTWALD SILBERRAD.

On examining Guyard's copper derivative (compare *Comptes Rendus*, 1884, xcvi., 526) the compound was found to be a cuprosamine periodide, $Cu_2I_2(5NH_4)_2I_2 \cdot H_2O$, and not a derivative of nitrogen iodide; it is not explosive, and has the properties of a periodide. On heating, it evolves iodine vapour, and by treating with potassium iodide solution the loosely combined iodine is removed quantitatively. The regeneration of nitrogen iodide from the cuprosamine periodide by ammonia must also be regarded as distinct evidence of its periodide character, for, according to this view, the loosely combined iodine reacts with ammonia precisely as does potassium periodide.

Cuprosamine Iodide, $Cu_2I_2 \cdot NH_3 \cdot H_2O$.—When the foregoing periodide is treated with potassium iodide solution, the loosely combined iodine is removed and a green crystalline residue remains behind, which dries to an olive-green crystalline powder having the above formula; it is insoluble in water, but dissolves fairly readily in ammonia.

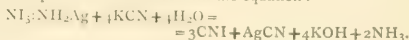
The silver derivative formulated by Szuhay as AgN_3 (Ber., 1893, xxvi., 1933) was again investigated, but it was found that by following his method a compound of constant composition could not be prepared. By the addition of iodine chloride solution to an ammoniacal silver solution, a pure product having the formula N_3NH_2Ag was obtained. The substance decomposes readily, even at the ordinary temperature and especially when exposed to light; in the dry state, it explodes on the slightest friction. It dissolves readily in potassium cyanide, and is regenerated by the addition of ammoniacal silver nitrate. Szuhay stated that an intermediate potassium salt was formed. This is disproved by an examination of the solution obtained by adding potassium cyanide to nitrogen iodide. Exactly 3 mols. of potassium cyanide were required to dissolve 1 mol. of nitrogen iodide, this number being independent of the excess of ammonia present. The pro-

ducts identified were cyanogen iodide, potassium iodide, potassium carbonate, potassium cyanate, ammonia, and cyanogen. The mechanism of the change is as follows :—



At low temperatures and in concentrated solution the cyanogen iodide is partially precipitated, but at the ordinary temperature it readily decomposes in solution.

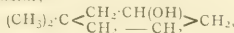
The action of potassium cyanide on the silver derivative took place in accordance with the equation :—



It was also found that although cyanogen iodide produced no precipitate of nitrogen iodide when added to ammonia, yet in the presence of silver the compound $N_3 : NH_2 \cdot Ag$ was readily obtained. The behaviour of the silver compound towards potassium cyanide is thus fully explained without any necessity for assuming the existence of an intermediate potassium salt.

*203. "Synthesis of 1:1-Dimethylhexahydrobenzene." By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

5-Chloro-3-keto-1:1-dimethyl-4-tetrahydrobenzene (Trans., 1903, lxxxiii., 117), when treated with sodium in moist etheral solution, yields 3-hydroxy-1:1-dimethyl-hexahydrobenzene, —



together with other substances not yet investigated. The product is a clear colourless liquid boiling at 99.5°/35 m.m., and having a marked odour of peppermint. When treated with fuming hydrobromic acid, it is converted into 3-bromo-1:1-dimethylhexahydrobenzene, a colourless liquid boiling at 98°/50 m.m. The bromine atom in this compound is readily replaced by hydrogen on heating with zinc dust in aqueous alcoholic solution, giving rise to 1:1-dimethylhexahydrobenzene, which is a colourless refractive liquid boiling at 117°/743 m.m., and having a geranium-like odour.

In 1902, Zelinsky (*Annalen*, 1902, cccxix., 318) described the preparation of dihydroisolarolene, which hydrocarbon, he suggested, was 1:1-dimethylhexahydrobenzene, and the authors are at present comparing the properties of these two hydrocarbons, and also the properties of 1:1-dimethyl-tetrahydrobenzene, with the hydrocarbons of the formula C_8H_{14} , which have at various times been obtained from derivatives of camphor.

*204. "The Formation and Reactions of Imino-compounds. I. Condensation of Ethyl Cyanoacetate with its Sodium Derivative." By HAROLD BARON, FREDERICK GEORGE PERCY REMFRY, and JOCELYN FIELD THORPE.

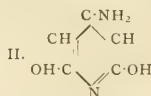
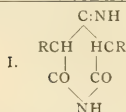
Ethyl cyanoacetate condenses with its sodium derivative, forming the sodium compound of ethyl α -cyano- β -imino-glutarate, $CO_2Et \cdot CHNa \cdot C(NH) \cdot CH(CN) \cdot CO_2Et$, which can readily be converted into ethyl α -cyano- β -imino-glutarate, $CO_2Et \cdot CH_2 \cdot C(NH) \cdot CH(CN) \cdot CO_2Et$. This substance contains three hydrogen atoms capable of replacement by sodium in the order indicated by the numerals.

Ethyl α -cyano- β -imino-glutarate and its alkyl derivatives yield the corresponding ethyl hydrogen salts, $CO_2H \cdot CHR \cdot C(NH) \cdot CR(CN) \cdot CO_2Et$, on hydrolysis with sodium carbonate.

These compounds, on heating above their melting points, are converted into derivatives of glutazine, which can be transformed into the corresponding derivatives of 2:4:6-trioxypyridine by suitable reagents.

The same glutazine derivatives are formed by the action of concentrated sulphuric acid on the diethyl salts.

The substitution derivatives of glutazine can react in the two forms :—



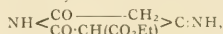
The mono-substitution derivatives react in the second form towards acid hydrolysing agents, and in the first form towards nitrous acid.

The di-substitution derivatives react only in the second form, whilst the tri-substitution derivatives react in the first form.

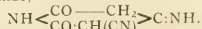
Ethyl α -cyano- β -iminoglutarate,—



can be converted into a derivative of glutazine in two ways. Thus, with concentrated sulphuric acid, it yields ethyl glutazincarboxylate,—



but with sodium carbonate solution it is converted into glutazine cyanide,—



*205. "The Affinity Constants of Aniline and its Derivatives." By ROBERT CROSBIE FARMER and FREDERICK JOHN WARTH.

The affinity constants of aniline and its derivatives are best determined through the hydrolytic dissociation of their salts. For this purpose, the method of distribution between two solvents, previously employed by one of the authors (Farmer, *Trans.*, 1901, lxxix., 863), has been applied to these compounds. The advantages of the method are, mainly, its applicability to (1) sparingly soluble organic compounds, (2) strongly coloured solutions, (3) solutions in which a slight decomposition interferes with titrations, (4) salts which are hydrolysed to the extent of nearly 100 per cent in solution.

Comparative experiments showed that the sulphates of aniline and the toluidines were in all instances hydrolysed to a greater extent than the corresponding hydrochlorides, but the relative difference decreased in dilute solution.

o-Nitroaniline showed practically no tendency to form a hydrochloride in aqueous solution, and *p*-nitroaniline was a much weaker base than the meta-isomeride. The nitroanilines exhibited no acidic properties when examined by the same method in presence of caustic potash.

The substituents arranged themselves in the following order as regards their influence on the affinity constant of aniline, the nitro-group being the most electronegative: NO_2 , CO_2H , $\text{N:N-C}_6\text{H}_5$, Br , Cl , CH_3 , OCH_3 . α - and β -Naphthylamines were somewhat weaker bases than aniline. Acetanilide and aceto-*o*-toluidide showed practically no basic properties. *p*-Nitrosomethylaniline possessed easily measurable acidic properties in addition to its basic properties, but *p*-nitrosodimethylaniline showed no tendency to form salts with alkalis.

206. "The Attractive Force of Crystals for like Molecules in Saturated Solutions." By EDWARD SONSTADT.

The author describes the preparation of saturated solutions in pairs or in sets, in which to one or more of the solutions is added a quantity of the crystals of the dissolved salt, the flasks or other containing vessels being left together in a cellar in which the temperature varies only slowly. The added crystals draw from the solution in which they are deposited a certain portion of the salt, so that the supernatant liquid contains, after a time, an appreciably smaller proportion of the dissolved salt than the solutions contained in the other vessels, to which no crystals had been added. The determinations were made either by evaporating a weighed portion of each of the solutions, and weighing the residue, or by taking the density of the solutions by a specific gravity bottle.

207. "The Grignard Reaction applied to the Esters of Hydroxy-Acids." By PERCY FARADAY FRANKLAND and DOUGLAS FRANK TWISS.

By acting on dimethyl tartrate with magnesium phenyl bromide and treating the product with dilute sulphuric acid, the authors have obtained a compound crystallising in small, white needles (m. p. 148°), which is presumably *aa\delta\delta*-tetraphenylerythritol, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{C}(\text{OH})(\text{C}_6\text{H}_5)_2$. It is powerfully dextrorotatory, a 4.327 per cent solution in ethyl alcohol giving $[\alpha]_D^{20} + 182.8^\circ$. The compound is isomeric with the already known benzoinsipinacone (tetraphenylerythritol, m. p. 235°).—

$\text{C}_6\text{H}_5 \text{CH}(\text{OH}) \cdot \text{C}(\text{OH})(\text{C}_6\text{H}_5) \cdot \text{C}(\text{OH})(\text{C}_6\text{H}_5) \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_5$ obtained by Kauffmann (*Chem. Centr.*, 1898, i., 1232) by the electrolytic reduction of benzil or benzoins, and which is, of course, inactive.

The authors, who are proceeding with the investigation, are making this preliminary communication in consequence of the incidental description by Acree (*Ber.*, 1904, xxxvii., 2753) of the action of magnesium phenyl bromide on inactive methyl mandelate with production of triphenylglycol.

208. "Note on the Addition of Hydrogen Cyanide to Unsaturated Compounds." By ARTHUR LAPWORTH.

Knoevenagel has recently stated (*Ber.*, 1904, xxxvii., 4065) that mesityl oxide unites nearly quantitatively with pure hydrogen cyanide, and in proof he cites the yield of mesitylic acid obtained by adding potassium hydroxide to the mixture after eight days and then boiling. As potassium cyanide, in presence of potassium hydroxide, rapidly converts mesityl oxide into mesitylic acid, Knoevenagel's experiment throws no light on the subject.

Experiments at 100° with hydrogen cyanide dissolved in alcohol are apt to be misleading, as after some hours at this temperature the solution is often faintly alkaline, and is much more reactive than before heating. The author has never obtained an appreciable amount of additive product when hydrocyanic acid free from all trace of basic impurity was warmed with an $\alpha\beta$ -unsaturated ketone; nevertheless, the views which he has put forward as to the mechanism of such processes are altogether opposed to the assumption that pure hydrogen cyanide is devoid of additive properties in any instance where addition occurs in presence of a base or a metallic cyanide (compare Knoevenagel, *loc. cit.*, p. 4067).

Alkylidenecyanoacetic acids react very readily with hydrogen cyanide in presence of bases or metallic cyanides; the products vary with the precise conditions imposed, but with care it is easy to obtain nearly quantitative yields of compounds derived from the type $\text{CHX}(\text{CN}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{H}$, and from which alkylsuccinic acids are produced by acid hydrolysis. For example, phenylsuccinic acid may readily be synthesised from benzaldehyde, potassium chloroacetate, and potassium cyanide. The study of this reaction as applied to both fatty and aromatic aldehydes is in progress. Alkylidenemalononic acids do not appear to be capable of uniting with hydrogen cyanide.

Wislicenus Memorial Lecture.

The Wislicenus Memorial Lecture will be delivered by Professor W. H. Perkin, F.R.S., on Wednesday, January 25th, at 8.30 p.m.

THE ROYAL SOCIETY.

Anniversary Meeting, November 30th, 1904.

THE Copley Medal was awarded to Sir WILLIAM CROOKES, D.Sc., F.R.S.; the Rumford Medal to Prof. ERNEST RUTHERFORD, F.R.S.; the Davy Medal to Prof. W. H. PERKIN, F.R.S.; and the Hughes Medal to Sir JOSEPH WILSON SWAN.

In presenting the Copley Medal the President, Sir WILLIAM HUGGINS, said:—

The Copley Medal is awarded to Sir William Crookes, F.R.S., for his experimental researches in chemistry and physics, extending over more than fifty years. Ever since his discovery of the element thallium in the early days of spectrum analysis, he has been in the front rank as regards the refined application of that weapon of research in chemical investigation. Later, the discrepancies which he found in an attempt to improve weighings, by conducting the operation in high vacua, were tracked out by him to a repulsion arising from radiation, which was ultimately ascribed by theory to the action of the residual gas. This phenomenon, illustrated by the radiometer, opened up a new and fascinating chapter in the dynamical theory of rarefied gases, which the genius of Maxwell, O. Reynolds, and others, has left still incomplete. The improvements in vacua embodied in the Crookes tube led him to a detailed and brilliant experimental analysis of the phenomena of the electric discharge across exhausted spaces; in this, backed by the authority of Stokes, he adduced long ago powerful cumulative evidence that the now familiar cathode rays, previously described by C. F. Varley, must consist of projected streams of some kind of material substance. His simple but minutely careful experiments on the progress of the ultimate falling off in the viscosity of rarefied gases, from the predicted constant value of Maxwell, at very high exhaustions, gave, in Stokes's hands, an exact account of the trend of this theoretically interesting phenomenon, which had already been approached in the investigations of Kundt and Warburg, using Maxwell's original method of vibrating discs.

These examples, not to mention recent work with radium, convey an idea of the acute observation, experimental skill, and persistent effort, which have enabled Sir William Crookes to enrich physical science in many departments.

In presenting the Rumford Medal the President said:—

The Rumford Medal is awarded to Professor Ernest Rutherford, F.R.S., on account of his researches on the properties of radio-active matter, in particular for his capital discovery of the active gaseous emanations emitted by such matter, and his detailed investigation of their transformations. The idea of radiations producing ionisation of the type originally discovered by Röntgen, and the idea of electrified particles, like the cathode rays of vacuum tubes, projected from radio-active bodies, had gradually become familiar through the work of a succession of recent investigators, when Rutherford's announcement of a very active substance, diffusing like a gas with a definite atomic mass, emitted by compound of thorium, opened up yet another avenue of research with reference to these remarkable bodies. The precise interpretation of the new phenomena, so promptly perceived by Rutherford, was quickly verified, for radium and other substances, by various observers, and is now universally accepted. The modes of degradation, and the enormous concomitant radio-activity of these emanations, have been investigated mainly by Rutherford himself, with results embodied in his treatise on radio-activity and his recent Bakerian lecture on the same subject. It perhaps still remains a task for the future to verify or revise the details of these remarkable transformations of material substances, resulting apparently in the appearance of chemical elements not before present; but, however that may issue, by the detection and description of radio-active emanations and their transformations, Professor Rutherford has added an unexpected domain of transcendent theoretical interest to physical science.

In presenting the Davy Medal the President said:—

The Davy Medal is awarded to Prof. W. H. Perkin, jun., F.R.S., for his masterly and fruitful researches in the domain of synthetic organic chemistry, on which he has been continuously engaged during the past twenty-five years.

Dr. Perkin's name is identified with the great advances which have been made during the past quarter of a century

in our knowledge of the ring or cyclic compounds of carbon. Thus, in the year 1880, the cyclic carbon compounds known to chemists were chiefly restricted to the unsaturated groupings of six carbon atoms met with in benzene and its derivatives, whilst the number of compounds in which saturated carbon rings had been recognised was very limited, and it was indeed considered very doubtful whether compounds containing carbon rings with more or less than six atoms of carbon were capable of existence.

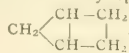
The starting point for Dr. Perkin's researches in this field of inquiry was his investigation of the behaviour of the di-halogen derivatives of various organic radicals with the sodium compounds of malonic, aceto-acetic, and benzoyl-acetic esters, which led to the synthesis of the cyclic polymethylene compounds up to those of hexamethylene, whilst heptamethylene derivatives were obtained by an adaptation of the well-known reduction of ketonic bodies leading to pinacones. The reactions thus introduced by Perkin are now classical, having proved themselves of the highest importance for synthetical purposes, and having been instrumental in stimulating the further investigation of the cyclic compounds of carbon.

Dr. Perkin also extended the same methods to the synthetical formation of carbon rings of the aromatic series, obtaining by means of ingeniously designed reactions derivatives of hydrindonaphthene and tetrahydronaphthalene.

But whilst the above achievements depend mainly on happily conceived and brilliantly executed extensions of the malonic and aceto-acetic ester synthesis, Perkin has, by a remarkable development of the Frankland and Duppa reaction for the synthesis of hydroxyacids, been successful in building up the important camphoric acid in such a manner as to place its constitution beyond doubt (1897).

Dr. Perkin has further devoted much attention to the important subject of the constitution of camphor, towards the elucidation of which he has contributed valuable experimental evidence embodied in a most important and elaborate paper, containing the results of many years' work in conjunction with numerous pupils, entitled "Sulphocamphylic Acid and Isolauronic Acid, with remarks on the Constitution of Camphor and Some of its Derivatives" (1898). Bearing on the same subject are later communications on camphoric acid and isocamphoric acid.

About the year 1900, Perkin, in prosecuting his researches on the constitution of camphor compounds, succeeded in devising synthetical methods for the production of what he has termed "bridged rings," of which a simple example is furnished by the hydrocarbon dicyclopentane



The universal admiration of organic chemists has been called forth by these investigations; they reveal, indeed, a wonderful capacity for devising reactions which coerce carbon atoms to fall into the desired groupings.

Of other publications displaying not only extraordinary experimental skill but close reasoning and the power of interpreting results, mention may be made of Dr. Perkin's memorable researches on the constitution of dehydracetic acid, berberine, brasilin, and hematoxylin respectively.

During the present year (1904), Dr. Perkin has made perhaps the most remarkable addition to the long list of his achievements by successfully synthesising terpin, inactive terpineol, and dipentene, substances which had previously engaged the attention of some of the greatest masters of organic chemistry.

In conclusion, it may be stated that Professor Perkin is not only the author of the above and numerous other important researches which are outside the scope of this brief summary, but that he has also created a school of research in organic chemistry, which stands in the very highest rank.

In presenting the Hughes Medal the President said:—

The Hughes Medal is awarded to Sir Joseph Wilson Swan, F.R.S., for his invention of the incandescent electric lamp, and his other inventions and improvements in the

practical applications of electricity. Not as directly included in the award, his inventions in dry-plate photography, which have so much increased our powers of experimental investigation.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 20, November 14, 1904.

The Employment of Helium as a Thermometric Substance, and its Diffusion through Silica.—Adrien Jaquerod and F. Louis Perrot.—It was proposed to use a helium thermometer to determine the melting-point of gold and the dilatation of some gases between 0° and 1000° . The gas, which was obtained from cleveite, was purified by passing it through copper oxide heated to dull redness and solid caustic potash. It was then mixed with about one-fourth of its own volume of oxygen and sparked for four or five hours. The excess of oxygen was absorbed by phosphorus. The gas, thus purified, gave only the characteristic lines of helium on spectroscopic examination; it was therefore quite pure. The gas was introduced into a thermometer with a silica bulb and heated. The temperature rose normally to the melting-point of gold, but the pressure of the gas, instead of rising regularly with the temperature, reached a maximum of about 900 m.m. and then began to fall. At 1100° it had fallen to atmospheric pressure, and went on falling regularly while the temperature remained constant. Its behaviour, therefore, was not due to leakage in the apparatus, but must be caused by diffusion of the gas through the silica. The rate of diffusion seems to be proportional to the pressure. Other experiments have shown that this diffusion takes place fairly rapidly at 510° , and is even perceptible at 220° .

Absorption of Hydrogen by Rhodium.—L. Quennessen.—Already inserted.

Action of Boric Acid upon Alkaline Peroxides and Formation of Perborates.—George F. Jaubert.—A mixture of crystallised boric acid and sodium peroxide was dissolved in cold water. After a short time white crystals separated out from this solution. Titration with KMnO_4 showed that these crystals contain 4.17 per cent of active oxygen, and their formula seems to be $\text{Na}_2\text{B}_2\text{O}_5 + 10\text{H}_2\text{O}$. By treating them with a mineral acid, a salt having the formula $\text{NaBO}_3 + 4\text{H}_2\text{O}$ was obtained. The latter does not decompose when kept dry, and since its solution in water yields hydrogen dioxide, it is a convenient reagent for the preparation of the latter.

Thioformic Acid.—V. Auger.—This acid was prepared in two ways:—1. By treating formic acid with NaPS_3 . It could not be obtained pure by this method. 2. From phenyl formate and sodium hydrogen sulphide, $\text{HCOOC}_6\text{H}_5 + \text{NaHS} = \text{C}_6\text{H}_5\text{OH} + \text{HCOSNa}$. The salt, precipitated by anhydrous ether, consists of long very deliquescent white needles. Its solution precipitates the salts of the heavy metals, giving unstable coloured salts.

Synthesis of $\beta\beta$ -Dimethyladipic Acid.—G. Blanc.— $\beta\beta$ -Dimethylglutaric anhydride, after being purified by crystallisation from petroleum ether, was reduced, and thus converted into the lactone, $\text{CH}_3 > \text{C} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_2 \end{smallmatrix} \text{CO} > \text{O}$. By heating this lactone to 275° with KCN, and by subsequent treatment, an acid having the formula $\text{CH}_3 > \text{C} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_2 \end{smallmatrix} \text{COOH}$ is obtained. This acid crystallises in little prisms which are very soluble in water, slightly soluble in benzene, and insoluble in petroleum ether. It melts at 87° . These properties show that it is identical with Tiemen's acid.

A New Sugar from Sorb Berries.—Gabriel Bertrand.—This sugar was first prepared in 1898 by Vincent and Meunier. They thought it contained 8 atoms of carbon. The author has shown that it is a hexavalent alcohol of formula $\text{C}_6\text{H}_{14}\text{O}_6$.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 15, 1904.

Varieties of Caoutchouc.—C. Harries.—The object of the author's research was to ascertain the connection between commercial caoutchouc and the juice as freshly obtained from the living tree. The fresh juice rapidly coagulates, and Weber has shown that ether extracts an oil from the latex which, on addition of traces of formic acid, polymerises to caoutchouc. Hence he supposes that the latex contains not caoutchouc as such, but a very easily polymerisable hydrocarbon, possibly an aliphatic diterpene, $\text{C}_{20}\text{H}_{32}$. The author obtained 300 c.c. of the juice of *Ficus magnol. Bori*, and treated it with ether on the spot, thus dissolving most of the constituents; a residue remained which contained a reducing sugar. The ether extract could be separated by filtration from the insoluble residue, which perhaps consists of albuminous substances. By the evaporation of the ether a yellow syrup was obtained from the extract; this partially crystallised on standing. By precipitation with alcohol it was shown that the extract consists of two substances:—(1) The substance which gives rise to caoutchouc, and (2) an oxygen compound, $\text{C}_{20}\text{H}_{46}\text{O}_3$. This latter crystallises well, and the greater part of it could be separated from the first by repeated treatment of the extract with a little ether. As the oxygen compound was thus removed it appeared that the other substance was not an oil, but a tough white elastic mass showing great resemblance to caoutchouc. It is perfectly soluble in a sufficient quantity of ether, but it could be shown that its properties are not those of a diterpene. On distillation it behaves exactly like caoutchouc. It may be precipitated directly from the latex by means of alcohol and purified by taking up with ether and precipitating with alcohol. Analysis shows that it has the composition of paracaoutchouc. If to the ethereal extract of the latex a drop of formic acid is added, a white coagulated mass separates at once. This product is soluble in ether, but loses its solubility gradually on drying or on repetition of the treatment. This gradual change of solubility (after isolation) is perhaps due to an increase in the molecule. Thus caoutchouc occurs in the latex of *Ficus magnol. Bori* (and also of *Ficus elastica*) in a form which differs in solubility from ordinary caoutchouc, but does not possess the properties of an aliphatic diterpene.

Separation and Isolation of Reducing Sugars by means of Hydrazine.—Emil Votocek and R. Vondracek.—Already noticed.

Antipodal Isomerism of Rhodose and Fucose.—Emil Votocek.—The author has proved his supposition that his rhodose and Tollens's fucose form an enantiomorphic pair, and has prepared from them the inactive sugar which is undoubtedly a true racemic body. This is the first case in which the stereoisomer of a natural sugar has been found in the free state. The fact that stereoisomeric sugars exist in nature is of great physiological interest; it shows, for instance, that the theory that nature only produces one of two enantiomorphic sugars is not universally correct. Thus the "directive force" which would cause the formation of only one series, e.g., the *d*-series, does not exist, though nature certainly produces this series far more commonly than the *l*-series.

Colloidal Silver Salts.—C. Paal and Franz Voss.—In continuing their researches on colloidal silver oxide the authors have found that if the silver salts of protalbinic or lysalbinic acid, which are formed when white of egg is subjected to alkaline hydrolysis, are dissolved in sodium carbonate solution, the excess of sodium carbonate removed by dialysis, and the liquid cautiously evaporated to

dryness, the sodium salt of the acid is formed and a colloidal silver carbonate. They have also prepared colloidal sulphide, chloride, bromide, and iodide of silver.

Microchemical Detection of Strontium and the Properties of Strontium Chromate.—W. Autenrieth.—On subjecting the salts of the metals of the alkaline earths to a microchemical examination the author has found that strontium chromate, when precipitated in neutral aqueous solution, very readily forms crystals. Barium chromate similarly prepared is amorphous or indistinctly crystalline, while calcium chromate is soluble in water. If one drop of a 10 per cent solution of potassium chromate is added to a 3 per cent solution of strontium nitrate, and the resulting crystals magnified 120 times, long yellow crystalline needles are seen, of length 100—200 μ and width 1 μ ; these collect together in clusters, and are very characteristic of strontium chromate. If the strontium solution is much weaker the crystals only separate out on standing for some time, and are then short thick hexagonal prisms. The author has not succeeded in getting spherical crystals as described by Behrens. The short thick crystals are also produced when a fairly dilute solution of strontium chromate in acetic acid or a mineral acid is allowed to stand for some hours after addition of excess of ammonia. Such a preparation on being kept for three months appeared to contain almost exclusively the crystals in the form of long needles. Thus strontium chromate possesses two crystalline modifications. The form which crystallises in thick prisms is probably the labile form, which appears to pass gradually into the stable modification crystallising in long needles. Strontium chromate when moist is easily soluble in acetic acid; when thoroughly dried at 120°, it is very slowly but completely dissolved. It is difficultly soluble even in boiling water. The easiest method of detecting barium, strontium, and calcium in presence of one another is to grind up the dry powdered chlorides repeatedly with absolute alcohol, and filter. Barium may then be detected in the insoluble portion by flame colouration, &c. The alcoholic filtrate is evaporated to dryness on the water-bath, the residue taken up with water, and filtered if necessary. Then a drop of potassium chromate is added to a drop of this solution, and examined under the microscope; the formation of characteristic long needles shows the presence of strontium. Calcium may be detected either spectroscopically or by means of the flame reaction, after evaporating the rest of the chloride solution with strong nitric acid, and separating the two nitrates by means of absolute alcohol.

Phosphorescing Zinc Sulphide.—W. P. Jorissen and W. E. Ringer.—The late De Visser has found that absolutely pure barium sulphide gives no trace of phosphorescence, while pure calcium sulphide only luminesces very feebly. By the addition of small quantities of bismuth powerful phosphorescence is produced, the maximum being reached when two atoms of bismuth are present in 100,000 atoms of barium or calcium; this effect is diminished by more as well as by less bismuth. De Visser states that in order that a sulphide may be capable of phosphorescing, it must contain in solid solution a compound of another metal which is in a state of electrolytic dissociation. The most refrangible radiations of the spectrum split up the ions of the foreign metal into a large number of electrons, which, by their vibration after illumination, cause phosphorescence. De Visser, whose experiments the authors are confirming and extending, examined many other metals, but discovered only a very few which could excite phosphorescence in the sulphides of calcium and barium. He thought it probable that many of these metals show invisible ultra-red or ultra-violet phosphorescence. He also found that the presence of some alkali salt in the sulphide was necessary for powerful phosphorescence, but no definite amount was required to cause maximum phosphorescence; he supposed that the alkali salt by fusing favoured the formation of the solid solution of bismuth in the calcium sulphide. Sidot's blende seems to behave in an exactly similar manner.

MISCELLANEOUS.

The Lavoisier Gold Medal has been awarded by the French Academy of Sciences to Professor Sir James Dewar, F.R.S., for his researches on the Liquefaction of Gases. This Medal was founded in 1900, to be given at such times as the French Academy should elect, in recognition of eminent services rendered to Chemistry by scientific men without distinction of nationality. It is the first occasion on which it has been awarded to a British man of science, the former distinguished Foreign Chemists being Fischer (of Berlin), Cannizzaro (of Rome), and Graebe (of Geneva).

International Book Circular.—We have received from Messrs. Williams and Norgate No. 139 of their International Book Circular; amongst other matters of interest it contains a special article by Dr. M. O. Forster, Assistant Professor at the Royal College of Science, entitled "Some Contemporary Foreign Chemists," together with an exact bibliography of their publications and a double plate of their portraits. The list comprises such well-known men as Richter, Ladenburg, Kiliani, Jüptner von Jonstorff, Beilstein, Liebermann, König, Barbier, R. Meyer, Kahlbaum, Roozeboom, van't Hoff, Von Baeyer, Biedermann, Berthelot, Erdmann, Fischer, Lunge, Ostwald, and Moissan. It is hardly necessary for us to point out the great value of such a publication, which Messrs. Williams and Norgate are willing to send to anyone on application.

MEETINGS FOR THE WEEK.

MONDAY, 19th.—Society of Arts, 8 (Cantor Lectures), "Musical Wind Instruments," by David James Blaikley.
TUESDAY, 20th.—Society of Arts, 8, "Street Architecture," by Thomas Graham Jackson, R.A.
WEDNESDAY, 21st.—Microscopical, 8, "Theory of Highly Magnified Images," by J. W. Gordon.

MR. EDWARD ARNOLD'S NEW BOOKS.

THE CHEMICAL SYNTHESIS OF VITAL PRODUCTS

AND THE INTER-RELATIONS BETWEEN ORGANIC COMPOUNDS
BY

R. MELDOLA, F.R.S., V.P.C.S., F.I.C., &c.,
Professor of Chemistry in the City and Guilds of London
Technical College, Finsbury.
Super Royal 8vo. 21s. net.

THE BECQUEREL RAYS AND THE PROPERTIES OF RADIUM.

By the Hon. R. J. STRUTT,
Fellow of Trinity College, Cambridge.
Demy 8vo. With Diagrams. 8s. 6d. net.

AN INTRODUCTION TO
THE THEORY OF OPTICS.
By ARTHUR SCHUSTER, Ph.D., Sc.D., F.R.S.,
Professor of Physics at the University of Manchester.
Demy 8vo. With numerous Diagrams. 15s. net.

THE ELECTRIC FURNACE.

By HENRI MOISSAN,
Professor of Chemistry at the Sorbonne.
Translated by A. T. de MOUILPIED, M.Sc., Ph.D.
Demy 8vo. With numerous Illustrations. 10s. 6d. net.

London: EDWARD ARNOLD, 41 & 43, Maddox St., W.

BIRKBECK COLLEGE,

Brems Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING ..	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board,
Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories

ABSOLUTE ALCOHOL,

FREE FROM DUTY,

FOR SCIENTIFIC AND RESEARCH WORK IN LABORATORIES

To be obtained from

HUGO LORENZ,

7-8, Idol Lane, Great Tower St., London, E.C.,

Licensed Trauer in Alcohol and Spirits of Wine.

Stock kept in suitable packages ready for immediate use.

ACETONE,

Chemically and Tech. pure.

METHYL-SPIRIT.**WOOD
NAPHTHA.****METHYLENE, Type Regie.****ACETON OIL.**

&c.

METHYLIC ALCOHOL

(Wood Spirit. Wood Naphtha).

MANUFACTURED BY

Stora Kopparbergs Bergslags Aktiebolag,

FALUN (Sweden).**E. GEORGE & SONS,**

BOOKSELLERS.

151, WHITECHAPEL ROAD, LONDON, E.,

Are OPEN to PURCHASE Complete Sets
or short runs of the following:—*Chemical News*, *The Analyst*
Journal of the Chemical Society, 1848 to 1870, *Journal of the Society*
of Chemical Industry, or the Publications of any other English or
Foreign Learned and Scientific Societies.—Libraries Purchased.

Current Catalogue of General Literature sent on application

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.

FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes

LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C.1, who hold stock ready for delivery**MELTING & BOILING-POINT
TABLES.**BY
THOMAS CARNELLEY,

D.Sc. (Lond.), B.Sc. (Vict.), F.C.S.,

Professor of Chemistry in University College, Dundee.

The Standard and only work upon the subject.

2 Vols. Ry. 4to. 799 pp. 42s.

HARRISON & SONS, Pall Mall, London, S.W.**SECOND EDITION.**

With Illustrations.

Price 2s. net (post free 2s. 1½d.)

Mdme. CURIE'S Thesis

ON

RADIO-ACTIVE SUBSTANCES.REPRINTED from the **CHEMICAL NEWS.****CONTENTS.**Introduction.—Historical.—Chap. I. Radio-activity of
Uranium and Thorium; Radio-active Minerals.—Chap. II.
Method of Research.—Chap. III. Radiation of the New
Radio-active Substances.—Chap. IV. Communication of
Radio-activity to Substances Initially Inactive.—Nature
and Cause of the Phenomena of Radio-activity.

16, NEWCASTLE ST., FARRINGDON ST., E.C.

COVERS FOR BINDING.Cloth, Gilt-lettered Covers for Binding the Half-yearly
Volumes of the**CHEMICAL NEWS**

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered
at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGDON ST., E.C.

BRYAN CORCORAN LIM.**MILLSTONE BUILDERS,**WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.Sole Makers of **MILBURN'S**

Patent Conoidal Stone Grinding Mills.

Especially suitable for certain materials, Wet or Dry.

Works and Warehouses: Back Church Lane.

Parcel Dept.: Basement of the Corn Exchange

31, MARK LANE, LONDON.**RECTIFIED SPIRIT**

(SPIRITS OF WINE).

B.P. and higher strengths. Duty paid; or
Duty Free under Finance Act 1902.**METHYLATED SPIRIT**Special Quotations to large
Institutions.**BOORD & SON,**

DISTILLERS SINCE 1750.

115-121 Tooley Street,

LONDON, S.E.

THE CHEMICAL NEWS.

VOL. XC., No. 2352

ELECTROLYTIC ANALYSIS OF COBALT AND NICKEL.*

ROBERT MOULTON PERKIN and W. C. PREBBLE.

CONSIDERING the large amount of work which has been done upon the electrolytic analysis of both cobalt and nickel, it might at first sight seem superfluous to endeavour to find any new methods or to undertake fresh work upon the subject. As a matter of fact our first experiments were not carried out so much with the object of finding new methods of analysis, but had for their aim the deposition of cobalt in a bright, and at the same time quantitative, manner.

All who have worked upon the electrolytic analysis of cobalt and nickel cannot fail to have been struck with the difference in appearance of the deposited cobalt and nickel. Thus, while it is easy to obtain brilliant deposits of nickel, which at the same time give quantitative analytical numbers, cobalt is usually dark and burnt in appearance, and the analytical results are almost invariably too high. It is strange that very few books dealing with electrolytic analysis refer to this remarkable difference between the two metals. Nor again, is any reference—as a rule—made to the fact that, whereas the deposited cobalt dissolves in moderately strong nitric acid with the greatest ease, the nickel deposit, although it may commence to dissolve readily, apparently becomes passive, and it is often extremely difficult to get the whole of the metal dissolved off the electrode. We will first of all describe the experiments undertaken with cobalt and leave those in connection with nickel to the end of the paper.

Cobalt.

In our first experiments, when attempting to obtain bright deposits of cobalt, thinking that perhaps the dark colour was due to slight superficial oxidation, we tried the effect of the addition of various reducing agents. The reducing agents tried were formaldehyde, formic acid, hydroxylamine, lactic, sulphurous, and hypophosphorous acids; the acids generally being employed in the form of their ammonium or sodium salts, and the solution kept alkaline by addition of ammonium hydrate. With the exception of hypophosphorous acid, the deposits obtained in presence of the reducing agents were extremely dark and sooty in appearance. But with sodium hypophosphite deposits of extraordinary brilliancy were obtained.

Sodium Hypophosphite.—The solution was made up by dissolving 5 grms. of ammonium sulphate and 1 grm. of the cobalt salt in a little water, adding 1.5 grm. sodium hypophosphite and 30 c.c. of ammonium hydrate (sp. gr. 0.88), the solution then being made up to 130 or 140 c.c. with distilled water. The mixture was then electrolysed with a C.D. of about 0.5–1.0 ampere per square decimetre, the temperature being kept at 35° to 40° C. Although the deposit obtained was extremely brilliant, the results were invariably too high, and did not even agree very well among themselves. The theoretical amount of metallic cobalt in cobalt ammonium sulphate, the salt used, is 14.94 per cent; the following three numbers show how far the results varied from the calculated value, 15.98, 16.26, and 15.84.

In order to ascertain, if possible, what caused these abnormal results, the deposits were dissolved in nitric acid and tested with ammonium molybdate. A voluminous yellow precipitate was produced, showing the presence of phosphorus. In fact the brilliant metallic deposit was a phosphor cobalt containing about 5 per cent of phosphorus.

We endeavoured to employ a somewhat similar solution to the one above described, for plating purposes, but found the deposit to be too brittle, so that we could not obtain deposits of any degree of thickness without the deposited metal exfoliating.

Acidulation of Cobalt and Tartrate.—A long series of experiments was then carried out, using solutions of the salts of various organic acids. The only two, however, which gave at all satisfactory results were ammonium oxalate and tartrate. From the point of view of appearance the tartrates give far better results than the oxalates; from quantitative considerations there is very little to choose between them. It will be noticed from the tables given that the results are almost invariably too high; this—in the case of tartrates—usually attributed to the presence of small quantities of carbon being deposited along with the metal. We consider that both with oxalates and tartrates traces of carbon are generally deposited along with the metal. In order to obtain a bright appearance a low C.D. should be employed until the bulk of the metal has been deposited. By attending to this condition the tartrates usually, but not invariably, give a very bright deposit, which at times has the appearance of burnished platinum. Generally speaking, with the oxalates the results obtained are not very bright, and the deposited metal is often very much burnt in appearance. Tables I. and II. give the results obtained by these two methods. The current density in all cases is calculated to 1 square decimetre of surface. Flag electrodes of platinum sheet were usually employed.

One very remarkable point in the electrolytic deposition of cobalt is, that sometimes a poor and unsightly deposit will give better analytical results than a bright one. Carrying out the electrolysis rapidly or slowly seems to affect the results very little. For example, in Table I. the last result but one from the bottom was carried out in less than two hours, and yet the amount of cobalt found was too high. On the other hand, all the results in Table II. which were conducted overnight were considerably too high.

Ammonia and Ammonium Borate.—A solution containing 3 to 4 per cent of ammonium borate and 30 per cent of ammonium hydrate (sp. gr. 0.88) was then tried. With this solution the resulting deposit is almost invariably brown and burnt, but as is seen from Table III., the analytical results are distinctly better than those obtained from solutions containing either the ammonium oxalate or tartrate. The borate solution was generally made up in bulk by dissolving 30 to 40 grms. of ammonium borate in 700 c.c. of water, and then making up to 1 litre with ammonium hydrate (sp. gr. 0.88). The cobalt salt was dissolved in about 50 c.c. of water, and from 30–50 c.c. of the above solution added to it, after which the solution was made up to the required volume and electrolysed. If during the electrolysis a black anode deposit was obtained, the addition of 5 or 10 c.c. of strong ammonia, or of 0.1 to 0.2 grm. hydroxylamine sulphate or hydrochloride, caused it to dissolve off, but the sulphate acts best.

It will be noticed that on one occasion the electrolysis was conducted for twenty-five hours, and on two others for twenty hours. This was not because such a long time is necessary to completely deposit the metal, but in order to see whether the results would be too high under these conditions; it will be seen that the length of time occupied in the electrolysis appears to have no influence upon the quantitative results.

Although the numbers obtained from the borate solution are a very decided improvement on those obtained from the other solutions already described, they still, from an analytical point of view, leave a good deal to be desired.

Phosphates and Free Phosphoric Acid.—We then tried a solution containing an alkali phosphate and a small quantity of phosphoric acid. With this solution very satisfactory results have been obtained; not only is the deposit bright, but the analytical numbers are also good.

In carrying out this process it was found that only a

* A Paper read before the Faraday Society, December 19, 1902.

TABLE I.—Five per Cent Ammonium Tartrate in Electrolyte.

Substance. Gms.	C. D. Amperes.	E.M.F. Volts.	Temperature.	Found.	Time.	Appearance
1'0357	0'6—0'7	4'3—4'4	30—40°	14'96	3'45"	Fairly bright
1'0215*	0'7	4'1	25—30°	14'73	2'24"	Brilliant
1'0867	0'9—1'4	3'7—5'0	50°	15'06	4'40"	Brown and burnt
0'7711	0—0'5	4'3	30—40°	15'13	4'35"	Fair
1'0000	0'4—1'0	3'9—5'0	30—40°	15'09	4'00"	Bright
1'0000	0'42—1'2	3'0—3'5	40	14'96	3'50"	Brilliant
0'5005	0'6—1'1	3'0—3'9	40	15'12	3'10"	"
0'5000	0'5—1'0	3'1	40°	15'00	4'10"	"
1'0000	0'3—1'0	3'0	Normal	15'10	All night	"
0'5000	0'25—1'0	3'15	"	14'94	"	"
1'0000	0'5—1'0	3'0—4'7	35°	15'00	5'00"	"
1'0136†	1'1—3'2	3'5—4'1	40—50°	14'92	2'55"	"
1'2920†	1'8—3'2	3'2—4'6	50—60°	15'05	1'55"	"
1'0000†	1'6—2'4	3'7—4'0	50°	14'95	2'35"	"

The theoretical percentage of cobalt in the salt taken, $\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, is 14'94.

TABLE II.—Five per Cent of Ammonium Oxalate in Electrolyte.

0'5000	0'3—0'4	0'3—3'5	40°	50'10	3'50"	Smoky
0'5000	0'64—1'2	2'7—3'3	30—40°	14'94	4'55"	Dark brown
0'5000	0'64—1'2	2'7—3'4	30—40°	15'08	4'33"	"
1'3897	0'8	2'8	30—40°	14'90	3'30"	"
1'0735	0'84	2'9	30—40°	14'91	5'25"	"
1'0015	0'2—0'3	2'2	Normal	15'15	All night	Fair
0'9987	0'2	2'5	"	15'13	"	Good
1'0038	0'2	2'6	"	15'17	"	Dull and streaky
1'0001	0'2	2'7	"	15'07	"	Badly burnt
1'0000	0'48	3'2	25°	15'09	4'50"	Milky appearance
1'0000	0'3	3'3	Normal	14'98	All night	Fair
1'3799	0'8—1'3	2'8—3'2	70°	15'06	4'00"	Burnt

TABLE III.—Solution containing Ammonia and Ammonium Borate.

0'9951	0'4—0'6	2'1—2'6	42—45°	15'07	6'00"	Brown
0'9990	0'4—0'44	2'3—3'1	50°	14'99	4'25"	"
0'9989	0'2—0'4	2'9—3'1	Normal	14'97	All night	Fair
0'9985	0'3	2'6	"	14'95	"	Brown
0'9969	0'2	2'1	"	15'18	25'	Very black
1'0004	0'28	2'7	"	14'96	All night	Burnt
0'9977	0'4—0'9	2'6—3'2	"	14'95	"	Streaky
1'0070	0'5	2'8	"	15'09	4'30"	Fair
0'7048	0'4	2'5	"	15'01	Night	"
1'0001	0'25	2'6	"	14'98	20'	Brown
1'0010	0'25—0'35	2'8—3'5	"	14'97	20'	"

TABLE IV.—Sodium Sulphate and Phosphoric Acid.

0'9994	0'35	2'4	Normal	14'87	All night	Brilliant
1'0009	0'2—1'0	3'0—4'0	"	14'94	"	"
0'9982	0'4—1'2	2'0—3'2	55°	14'90	4'50"	"
1'0016	0'2—0'6	3'0—3'2	Normal	15'02	All night	"
1'0000	0'4—1'1	2'2—3'75	58°	14'96	3'50"	"
1'0000	0'4—1'5	2'2—4'0	55	14'89	5'50"	"
1'0000	0'4—1'2	2'4—3'3	55	15'00	4'10"	"
1'0000	0'4—1'0	2'5—3'2	55	14'96	7'00"	"
1'0000	0'6—1'0	3'0—3'5	60	14'87	6'00"	"
1'0000†	0'3—1'0	2'5—3'3	63	14'98	2'40"	"
1'0000	0'4—1'0	2'2—3'7	60	14'97	6'00"	"

TABLE V.—Ammonium Borate and Ammonia.

0'9991	0'32	2'6	Normal	14'88	All night	Dead silver white
1'0372	0'30	2'4	"	14'84	"	"
1'0000	0'5	2'5	"	14'86	6'00"	"
1'0000	0'5	2'7	"	14'90	6'00"	"
1'0005	0'5	2'7	30—40°	14'84	5'00"	"
1'0000	0'1	2'3	Normal	14'90	All night	"
1'0000	0'3—0'4	2'1—4'0	20—40°	14'86	9'00"	"
1'0000	0'3—0'8	2'3—3'2	40	14'84	9'30"	"
1'0002	0'2—0'3	2'0—3'1	50	14'87	8'00"	"
1'0000	0'3—0'8	2'1—3'2	40°	14'89	6'50"	"
1'0000	0'3—0'9	2'3—3'25	40°	14'86	6'30"	"

* Time too short.

† Rotating cathode.

TABLE VI.

Substance.	C. D. Amps.	E.M.F. Volts.	Temp.	Time	Remarks
1'00000	0'3—0'08	2'0—3'0	Normal	14'0	23 hours Dead silver white
1'00000	0'3—0'2	2'25—3'0	"	14'1	21 " " "
1'00000	0'3—0'07	2'1—3'2	"	14'61	5 " " "
1'00000	0'15—0'3	2'1—3'0	Normal	14'63	22 " " "

TABLE VII.—Solution containing 3 grams. Ammonium Tartrate

1'00000	0'3—0'08	2'6—4'0	50	14'86	24 hours	Fair
1'00000	0'2—1'04	2'3—4'0	55	14'72	5 "	Good
1'00000	0'2—1'0	2'8—4'0	50	14'87	6 "	Very good
1'00000	1'0—1'1	1'3—5'0	40	15'02	4 "	Burnt
1'00000	0'2—1'0	2'7—4'0	55	14'87	7 "	Very good
1'00000	0'25—1'2	2'65—4'0	51	14'92	7 "	Burnt
1'2298	0'2—0'3	3'0—3'1	Normal	14'88	20 "	Good
1'00000	0'1—0'07	2'8—2'9	"	15'08	18 "	"
1'1400	0'2—1	3'5—4'0	40	15'05	5 "	Fair

small quantity of ammonium or sodium phosphate may be added; otherwise, the double salt of cobalt and the alkali phosphate is precipitated, and when once precipitated it can only be re-dissolved again with great difficulty. The following method of procedure gave the most satisfactory results:—About 1 gm. of the cobalt salt was dissolved in about 50 c.c. of distilled water, and then 5 c.c. of a 5 per cent solution phosphoric acid added. To this solution 25 c.c. of a 10 per cent solution of ammonium dihydrogen phosphate, $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, or better, sodium dihydrogen phosphate, $(\text{NaH}_2\text{PO}_4)$, was added; the solution was then made up to 130 c.c. and electrolysed, a gauze flag electrode being employed as cathode. After the electrolysis has proceeded for half-an-hour or so there is usually a brown deposit of cobalt oxide on the anode. In order to dissolve this deposit off, about 0.5 gm. of hydroxylamine sulphate or chloride is added to the solution, when the deposit almost immediately vanishes. Very often 0.1 gm. of the hydroxylamine salt is quite sufficient. The addition of a few c.c. of formaldehyde solution has the same effect, but the action is much slower. The anode deposit is much more marked when hot solutions are electrolysed, but there is no difficulty in removing it as already described. If the solution is heated to too high a temperature, there is a tendency for the double salt of sodium and cobalt phosphate to be precipitated out. The phosphoric acid is added in the first place to prevent the precipitation of this double salt, because if it is once precipitated a considerable quantity of phosphoric acid must be added in order to dissolve it again. But when there is too much phosphoric acid in the solution the deposition of the cobalt is extremely slow. It is, in fact, always an advantage, after the bulk of the cobalt has been deposited, to add a few drops of very dilute ammonium hydrate to neutralise the excess of acid liberated by the electrolysis. The last examples in the table only had 1.3 c.c. of a 5 per cent solution of phosphoric acid added, which is only about 0.02 per cent (the volume was 130 c.c.); in such cases it is not necessary to neutralise with ammonia.

It will be noticed that by employing this method for depositing cobalt, the whole of the metal can be thrown out in from three to three and a-half hours, which is considerably quicker than by any other method. It is advisable to start with a low-current density, and to increase this after the electrolysis has been proceeding for about an hour.

Nickel.

The electrolytic analysis of nickel salts from solutions containing ammonium sulphate and free ammonia is so very satisfactory that it hardly seemed worth while to try any new solutions for the analysis of this metal. In spite of this, we thought that it would be interesting to see how nickel would behave when electrolysed in solutions containing ammonium borate and ammonia, and from solutions containing an acid phosphate and phosphoric acid. With ammonium borate and ammonia the results are

extremely satisfactory. Recently, Taggart has published a paper upon the deposition of nickel from solutions containing disodium hydrogen phosphate and phosphoric acid (*Trans. Am. Chem. Soc.*, xxv., 1939). Taggart employed rather larger quantities of phosphoric acid than we have found satisfactory. He used a platinum basin as the cathode, and found it necessary to wash repeatedly down the sides of the basin to prevent the double salt of nickel and sodium phosphate from crystallising out, a proceeding which, to say the least of it, is tiresome. The results which he publishes are certainly very satisfactory.

In working on the same lines as those we found so successful in the case of cobalt, viz., adding a little free phosphoric acid to the nickel salt before adding the sodium dihydrogen phosphate and electrolysing the resulting solution, we did not obtain satisfactory results. There was a very great difficulty in depositing the last traces of the nickel, and from about thirty experiments we only obtained one really satisfactory result. We cannot therefore recommend the phosphate solution as being satisfactory for the electrolytic analysis of nickel.

Ammonium Borate and Ammonia.—We have already shown that although cobalt gives very fair analytical numbers from solutions containing ammonium borate and ammonia, the appearance of the deposit leaves very much to be desired. With nickel the analytical results, from a quantitative point of view, are magnificent, and although the deposited metal has not the brilliant burnished appearance often obtained by other methods, it is not unsightly, having a matt silver-greyish appearance. In Table V, we give some of the analytical results obtained, and from them it will be seen that from an analytical point of view no better method could be devised. The salt employed was nickel ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 5\text{H}_2\text{O}$, which contains 14.87 per cent of nickel.

As showing the exactness of the method the numbers in Table VI, obtained from a sample of ammonium nickel sulphate which had been imperfectly dried, are of interest. A 5 per cent solution was made up, and for each analysis 20 c.c. of this solution, containing 1 gm. of the salt, was taken.

Table VII. shows a series of results obtained with ammonium tartrate. With care this method can be caused to give very good quantitative yields, but the results are apt to be erratic. It is advisable to keep the current density fairly low.

From the results of our work it is clear that, although there are several methods which may very satisfactorily be employed for the electrolytic analysis of nickel, the only really satisfactory one for analysing cobalt is the one containing phosphates and free phosphoric acid. It is very remarkable that this method should, however, not give satisfactory numbers when employed for the analysis of nickel. But, so far as general analysis is concerned, even the methods which give slightly high results with cobalt

are more satisfactory than the gravimetric processes for analysing this metal, which are employed in pure chemistry.

We have not yet succeeded in devising a satisfactory electrolytic method for the separation of cobalt and nickel, and have not found the methods described in the literature to give really reliable results.

Some of the results in Table I. are due to Mr. E. G. P. Bousfield, to whom our thanks are due.

Borough Polytechnic Institute, London
Electrochemical Laboratory.

THE ELECTROLYTIC SOLUTION OF PLATINUM.

By ANDRÉ BROCHET and JOSEPH PETIT

Acids are without action on platinum; aqua regia alone dissolves it, and this mode of attack, due to the formation of chlorine, is relatively slow if the metal has been melted or rolled.

Platinum utilised as an anode is unattackable in most cases; the electrolysis of hydrochloric acid and of the chlorides, however, has an action which is far from being negligible.

The transformation of the chlorates into perchlorates is accompanied by transportation, more or less distinct, from the anode to the cathode.

(*Zeit. f. Elektrochemie*, 1903, vol. ix., p. 235), who found that the addition of a continuous current to the alternating one caused the platinum to be dissolved to an appreciable extent. An analogous result was obtained by using the alternating current in the presence of oxidising agents, particularly chromic acid.

Following up our researches on electrolysis by means of alternating currents (*Bull. Soc. Chim.*, [3], 1904, vol. xxxi., p. 359), we decided to examine the solution of platinum in the cyanides, a solution which is of much more importance than that mentioned by the preceding authors.*

We have already examined the electrolysis of cyanide of potassium with an anode of platinum. We know that under these conditions the metal is completely insoluble; it is a strip of platinum that is used as the anode in hot gilding, and the operator plunges this electrode in, to a greater or less extent, according to the intensity of the current and the effect of colouration he desires to obtain. Cyanide of potassium is decomposed with the formation of potash, ammonia, and carbonic anhydride.

Cyanide of Potassium.—For the examination of the solution of platinum under the influence of an alternating current, we have made use of a small narrow apparatus in which are placed two strips, 1 c.m. in width and 0.1 m.m. in thickness, dipping 5 c.m. into the electrolyte. This latter consisted of a solution of cyanide of potassium at 4 grm.-molecules per litre (15 c.c.).

Too rapid heating, caused by the high density of the

TABLE I.—Solution of Platinum in Cyanide of Potassium. Influence of the Density of the Current.

Surface of the Electrodes, $5 \times 1 = 5$ sq. c.m.; Strength of Solution, 4 grm.-molecules per Litre.

Temperature	Intensity.		Density of current.	Time in minutes	Platinum dissolved.			Return, per cent
	Eff. Amperes	Mean. Amperes			Found. M.grms.	Calculated. M.grms.	Per ampère-hour	
10–12°	1'1	1	20	10	62	606	372	10'2
18–21°	2'2	2	40	10	172	1212	516	14'2
23–27°	3'3	3	60	5	137	910	548	15'0
32–36°	4'4	4	80	5	202	1212	606	16'7

TABLE II.—Solution of Platinum in Cyanide of Barium. Influence of the Density of the Current.

Surface of the Electrodes, 6 sq. c.m.; Strength of Solution, 2 grm.-molecules per Litre.

Temperature.	Intensity.		Density of current.	Time in minutes.	Platinum dissolved.			Return, per cent
	Eff. Amperes	Mean. Amperes			Found. M.grms.	Calculated. M.grms.	Per ampère-hour	
15°	0'92	0'83	14	10	17	503	265	7'4
18°	2	1'8	30	15	161	1640	358	9'8
18°	3	2'7	45	10	158	1640	352	9'6
18°	4	3'6	60	5	120	1092	400	11'0

De la Rive (*Comptes Rendus*, 1837, vol. iv., pp. 835 and 909) observed that if we pass an alternating current through a sulphuric acid voltameter, the electrodes become rapidly changed; there is no solution effected, but simply the formation of platinum black.

This manner of behaving with an alternating current has been confirmed by other writers who have studied the question. Drechsel (*Journ. f. Prakt. Chem.*, [2], 1879, vol. xx., p. 378; 1880, vol. xxii., p. 476), when examining the hydration of carbonate of ammonium under the influence of an alternating current, observed the solution of the platinum and the formation of different salts (*Journ. f. Prakt. Chem.*, [2], 1882, vol. xxvi., p. 257) which were examined by Gerdès.*

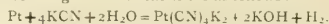
More recently, Margules (*Ann. der Chemie und Physik*, [2], 1898, vol. lxxv., p. 629; vol. lxxvi., p. 540) undertook, in a purely qualitative manner, the examination of the action of the alternating current on platinum in the presence of various electrolytes; his researches were resumed by Ruer

current, was prevented by placing the apparatus in a recipient full of water.

The results obtained are given in Table I. The return is obtained, as in our previous researches, from the ratio between the weight of platinum dissolved and the weight calculated for the total amount of electricity passing through the apparatus during the time of the experiment.

We see from Table I. the importance of the solution as soon as we exceed half a grm. per ampère-hour.

On continuing the action of the current the strips of platinum gradually dissolve, the liquor becomes heated, and, on cooling, the colourless solution deposits yellow crystals of platino-cyanide of potassium, appearing green by reflected light. The reaction is as follows:—



With a density of current of 40 ampères per square decimetre, we can dissolve approximately a thickness of 1/10th of a m.m. per hour; with 80 ampères only twenty-five minutes are required.

Cyanide of Barium.—Platinum behaves in the same

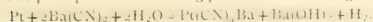
* Dannel (*Zeit. f. Elektrochemie*, 1890, vol. vi., p. 275) mentioned the preparation of identical salts by Erdmann. He gave no reference, however, and we have not been able to find the paper. We are, however, of the opinion that the work, attributed by mistake to Erdmann, is none other than that of Gerdès.

* Let us remark that when operating under the ordinary conditions of our experiments, the solution of platinum in hydrochloric acid is about 1 per cent, or about 0.04 grm. per ampère-hour.

manner in a solution of cyanide of barium. Our experiments were carried out on wire 2 m.m. in diameter, plunged about 9 c.m. into a solution of cyanide of barium containing about 2 gm.-molecules per litre. We obtained the results shown in Table II.

As with cyanide of potassium the solution is effected very easily, but with a smaller return. The solution remains perfectly colourless, but it soon becomes cloudy owing to the formation of carbonate of barium.

The principal reaction taking place is the following:—



As in the electrolysis by means of a continuous current, there is a decomposition of the cyanide, with the formation of carbonic anhydride and ammonia.

We have also observed the production of nitric acid, collected in the last residuary waters in the form of nitrate of barium.

If the solution becomes heated, the hydrate of barium and the platino-cyanide remain in solution, and are deposited on cooling.

Conclusions.—Platinum, therefore, is dissolved easily in cyanides under the influence of an alternating current. This point is the more interesting as this metal offers a special resistance to chemical reagents.

The cause of this solution, which could not have been predicted, appears to us to be of great theoretical interest. Our researches have led us to the establishment of a process for the manufacture of platino-cyanides, particularly that of barium, of which we propose to give fuller details later on.

We will simply remark here that the present process consists in forming successively platonic and platinous chlorides, and platino-cyanides of potassium and of copper. Finally, this latter salt is treated with baryta water.

These operations are long and troublesome on account of the impurities which have to be eliminated.

By our method the platinum is dissolved directly in the cyanide of barium, it suffices then to filter and crystallise the salt.

As for the amount of electric energy used, it is very small; it corresponds approximately to eight kilowatt-hours per kilogram. of platino-cyanide of barium obtained. —*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 12.

HYDRONITRIC ACID AND THE INORGANIC TRINITRIDES.*

R. I. M. DENNIS and A. W. BROWN†

(Continued from p. 308.)

II. EXPERIMENTAL (continued).

(b) The Preparation of Sodium Trinitride from Sodium Amide.

In his original work upon the method, W. Wislicenus (*Ber.*, xxv., 2084) prepared sodium trinitride by passing nitrous oxide over sodium amide heated to a temperature of between 150° and 250°. He obtained a yield equal to 50 per cent of the theory called for by the equation $3\text{NaNH}_2 + \text{N}_2\text{O} = \text{NaOH} + \text{NaN}_3 + \text{NH}_3$.

Szarvasy (*Journ. Chem. Soc.*, lxxvii., 603) worked between the temperatures of 190° and 220° and obtained a yield of 56 per cent.

In the early work done in this laboratory the temperature varied between 210° and 225°. As the thermometer was usually from 1 to 3 inches above the nickel dish in the iron can, the actual temperature of the amide was probably somewhat higher. In one experiment the attempt was made to bring the bulb very close to the surface of the amide. As a result, the bulb broke during the course of the experiment, probably because it came in contact with the molten amide, and the mercury upon dropping into the amide caused a violent explosion that completely

wrecked the apparatus. The best method of securing accurate temperature measurement in this work would probably be to encase the thermometer bulb in a polished nickel tube, closed at the lower end, and then submerge it in the molten amide. In our later work, however, the thermometer was simply placed outside the nickel dish within the can, so the bulb was on a level with the amide.

In this way fairly accurate measurements were possible.

The yields of sodium trinitride obtained in the early work here were very low, seldom rising above 5 per cent of the theory, even when the amide used was of a high grade of purity. Consequently, some years ago Mr. Edward Hirshfield undertook, in this laboratory, a careful study of the process, and found that the low yield was not attributable either to leakage of air or moisture into the apparatus, or to the catalytic action of the nickel crucible.

Mr. Hirshfield then noticed that small portions of the product adhering to the bottom of the inlet tube were of an appearance quite different from that of the rest of the mass, and showed a percentage of sodium trinitride in one case equal to 79 per cent of theory, while the main mass showed no more than 2 per cent. This at once suggested a consideration of the influence of temperature upon the reaction. The product scraped from the inlet tube had undoubtedly been formed at a lower temperature than that to which the contents of the crucible had been subjected. It had a crumbly appearance, as though it had solidified as soon as formed, while the contents of the crucible gave the appearance of having been perfectly fused.

A series of four experiments was now conducted in which, to facilitate observation and to enable quick regulation of temperature, a long combustion tube, bent upwards at the ends, was used. In each case a quantity of the amide, broken into small pieces, was introduced into the tube, which was then cautiously heated in a combustion furnace until the amide was in a state of perfect fusion. As anticipated, the greenish liquid began slowly to change to a white solid, the transformation beginning at the end of the tube nearest the nitrous oxide generator and proceeding toward the other end. If during the process any portion of the tube became slightly overheated, there would result a violent rush of gas and a local ignition confined to the limited area that has been overheated. This could instantly be checked by shutting off the supply of nitrous oxide. The results of these four experiments are shown in Table III. In Nos. 1, 2, and 3 several local ignitions were observed to take place. In No. 4 their occurrence was prevented by regulating the temperature with extreme care.

TABLE III.

	Grms. AgCl per gm. product	Percentage yield of NaN ₃
1	1.0086	74.0
2	1.1177	82.0
3	0.9405	69.0
4	1.2376	90.8

The results of these experiments seem to show that the low yield in the previous runs was due probably to the secondary reaction between nitrous oxide and sodium trinitride, this action taking place with almost explosive violence at temperatures above a certain limit, and to some slight extent perhaps even at comparatively low temperatures.

To further test this assumption, Mr. Hirshfield conducted several experiments upon weighed amounts of carefully prepared sodium trinitride. In each case the substance was placed in a porcelain boat and introduced into a combustion tube as close as possible to the bulb of the thermometer. Heated for one hour in a current of nitrous oxide to a temperature of between 200° and 205°, the sodium trinitride remained unchanged in appearance except that it became slightly darker. Analysis showed, however, that it had lost about 5 per cent of its nitrogen. In another experiment the temperature was gradually

* From the *Journal of the American Chemical Society*, xxxvi., No. 6.

raised. Before fusion could take place there was a bright ignition, accompanied by a violent rush of gas. A small amount of metallic sodium sublimed along the walls of the tube, and the boat, which had been considerably attacked during the experiment, was found to contain a white substance, soluble in water, and yielding fumes of nitrogen peroxide on acidification with sulphuric acid. In the next experiment care was taken to free the nitrous oxide from any of the higher oxides of nitrogen that it might contain by passing it through a strong solution of potassium hydroxide. Notwithstanding this precaution, acidification of the product with sulphuric acid gave the same result as before. Tests for hyponitrites gave negative results. The product was finally decided to contain sodium nitrite, which was probably formed in accordance with the equation $\text{NaN}_3 + 2\text{N}_2\text{O} \rightarrow \text{NaNO}_2 + 3\text{N}_2$.

When heated in a current of pure nitrogen, sodium trinitride was decomposed before it reached its melting-point. The process of decomposition was accompanied by a violent evolution of gas, but by no ignition. Only metallic sodium remained in the boat.

As a consequence of these experimental results the temperature of 190° was adopted by the authors for the conversion of sodium amide into sodium trinitride. The temperature may be allowed to vary 3° or 4° from this point without materially influencing the result.

In the hope of shortening the process by increasing the surface of contact between the reacting substances, as was done in the preparation of sodium amide, the attempt was made to bubble the nitrous oxide through the molten amide. Two experiments convinced us that this could not be done without stoppage of the inlet tube, due to the formation there of the solid products of the reaction.

To determine the percentage yield of sodium trinitride, the product is dissolved in considerable water barely acidified with sulphuric acid and made up to a known volume. In measured portions of this solution the hydronitric acid is then determined by the method of Dennis (*Journ. Am.-Chem. Soc.*, 1896, xviii., 947). This consists in precipitating the hydronitric acid with silver nitrate, collecting the silver trinitride upon a hardened filter, washing with cold water until the wash-water gives no reaction for silver, dissolving the precipitate upon the filter with dilute, hot nitric acid, adding hydrochloric acid to the solution thus obtained, and collecting and weighing the resulting silver chloride. This method was used in obtaining the results given in Table III. Curtius (Curtius and Rissom, *Journ. Prakt. Chem.* [2], lviii., 261) determined hydronitric acid by distilling the substance to be analysed with sulphuric acid, and catching the distillate in a measured excess of tenth-normal potassium hydroxide solution. Other volatile acids must, of course, be absent. West (*Journ. Chem. Soc.*, lxxvii., 705) modified the method of Curtius by using a measured excess of tenth-normal sulphuric acid to drive off the hydronitric acid from the solution of (say) its sodium salt. The amount of sulphuric acid used was then determined by titrating back with tenth-normal sodium hydroxide. Here, again, no volatile acid other than hydronitric acid may be present.

(c) The Preparation of Hydronitric Acid from Sodium Trinitride.

To prepare free hydronitric acid the aqueous solution of the mixture of sodium hydroxide and sodium trinitride, obtained by the action of nitrous oxide upon sodium amide, is placed in a distilling flask and a few drops of litmus solution are added. A separatory funnel is then inserted in the neck of the flask and the side tube is connected with a condenser, and the condenser with a receiving flask containing a little water. The solution is then heated nearly to boiling, and sulphuric acid (1 : 1) is slowly introduced through the separatory funnel until the acid is in excess. Distillation is continued as long as the distillate gives the reaction for hydronitric acid with silver nitrate.

SUMMARY.

For the convenience of the reader the method for the preparation of hydronitric acid that has finally been adopted as the result of our examination of the process may be summarised as follows:—

One hundred grms. of metallic sodium are placed in a nickel dish and heated in the iron can, previously described, to a temperature of about 350° in a current of pure ammonia gas, that is first dried by passing it through soda-lime and fused sodium hydroxide. During this process the temperature must not be allowed to fall below 250° . The inlet tube, through which the ammonia enters, is pushed down beneath the surface of the sodium as soon as that metal melts, so that the gas may bubble up through the liquid. When the reaction is nearly complete (from five to seven hours) the inlet tube is raised out of the liquid. The flow of ammonia gas should be steady to prevent the rise of sodium in the inlet tube. In any case it is well to guard against the danger due to sudden stoppage by providing the inlet tube at some point outside of the iron can with a perpendicular side tube dipping into mercury. The end of the reaction is shown by the absence of hydrogen in the gas escaping from the can. Hydrogen in this escaping gas may be detected by collecting the gas in a test-tube by displacement, closing the tube with the thumb, and immersing the mouth of the tube in water to absorb the ammonia, and then bringing the residual gas in the test-tube into contact with a flame. When no inflammable gas is present in the tube, the operation may be regarded as complete. The apparatus is then allowed to cool nearly to the temperature of the room. It has been found inadvisable to treat all of this product in one operation with nitrous oxide because of the tendency to "creep" shown by the sodium trinitride. Consequently, about three-fourths of the sodium amide resulting from the above operation is removed and placed in a desiccator over metallic sodium.

The iron can containing the remainder of the sodium amide in the nickel dish is now connected with an apparatus furnishing dry nitrous oxide, the arrangement

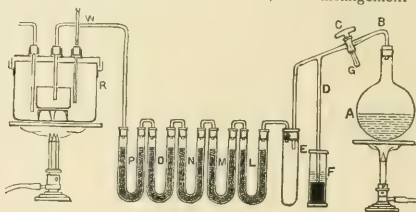


FIG. 2.

being that shown in Fig. 2. This gas is made by heating ammonium nitrate. The ammonium nitrate is contained in the flask A resting on an iron plate and heated by a single Bunsen burner. The outlet tube B slopes downward and carries a two-way stop-cock, C, and the branch tube D, and at the end is bent down and inserted in a test-tube, E. The test-tube D is about 30 c.m. long and is immersed to the depth of not more than 1 c.m. in mercury that stands in the bottom of the small cylinder, F. This arrangement serves to collect in F water that may flow down the side tube D, and furnishes also a safety-valve for the release of pressure whenever stoppage occurs in the tube W. The object of this device is to catch most of the water evolved in the decomposition of the ammonium nitrate, preventing, on the one hand, the passage of the large amount of moisture into the drying agents beyond, and on the other hand, the return flow of the condensed moisture into the flask A. During the operation the two-way stop-cock C stands in such a position that the flask communicates with the drying agents beyond. Whenever

it is desired to stop the flow of nitrous oxide through the apparatus, the stop-cock is turned to such a position as allows the escape of the gas through its lower end. The test-tube *E* serves to collect the condensed water that may have passed beyond the side arm *D*. The outlet tube from *E* is connected with U-tubes, *L*, *M*, containing soda-lime, and beyond these are three U-tubes, *N*, *O*, *P*, containing fused sodium hydroxide. The gas then enters the inlet tube *W* of the apparatus *R*, which has already been shown in Fig. 1.

The generation of the nitrous oxide is now begun, and when all air has been displaced from the apparatus the iron can is heated to a temperature of 190° . In this part of the operation the gas is not bubbled through the molten amide, because the product is solid and would cause stoppage of the tube. The conversion of the 25 grms. of sodium amide takes about five hours. The end of the reaction is indicated by the absence of ammonia in the gas escaping from the outlet tube of the can. When the conversion is complete, the flame under the can is extinguished and the contents of the nickel dish is allowed to cool in a current of nitrous oxide. The cold product, consisting of a mixture of sodium trinitride and sodium hydroxide, is then dissolved in water. Hydronitric acid is distilled off in the manner previously described.

If the process has been properly conducted, no gas will be evolved when the final product is dissolved in water.

B.—The Composition of Lithium Inorganic Trinitrides.

Lithium Trinitride and Barium Trinitride. In the course of the investigation by Dennis and Doan (*Journ. Am. Chem. Soc.*, xviii., 970) upon the compounds of thallium a large amount of pure hydronitric acid had been prepared by a modification of the Wislicenus method, but no systematic study of the compounds of the acid with inorganic bases was entered upon because of the expressed reservation of this field by Curtius (*Journ. Prakt. Chem.*, xliii., 208) in 1891. When, however, seven years had elapsed without the appearance of any publication by Curtius on the inorganic trinitrides, it was thought that this branch of the field might, without discourtesy to the discoverer of hydronitric acid, be regarded as open to other investigators. Consequently, there appeared in 1898 an investigation carried on in this laboratory by Dennis and Benedict (*Journ. Am. Chem. Soc.*, xx., 225; *Zeitschr. Anorg. Chem.*, xvii., 18) upon the salts of hydronitric acid. Curtius, however, had evidently considered that his reservation of this field was a perpetual one, for, in an article with Rissom (*Journ. Prakt. Chem.*, 1898, lviii., 261) upon the inorganic trinitrides, published shortly after the appearance of the investigation by Dennis and Benedict, he courteously refers to their work in the following words: "In neuester Zeit, nach dem Abschlusse unserer Untersuchungen haben Dennis und Benedict mitgeteilt, dass sie das Bedürfnis gefühlt haben, 'ein systematisches Studium der Verbindungen der Stickstoffwasserstoffsäure' zu beginnen und in einer Abhandlung die Resultate mitgeteilt (*Zeitschr. Anorg. Chem.*, xvii., 18), welche sie bei der Untersuchung der Elemente der Alkali- und Erd-alkalimetalle erhielten."

Dennis and Benedict prepared the trinitrides of lithium, sodium, potassium, rubidium, and cesium by dissolving the respective hydroxides in hydronitric acid, and the trinitrides of calcium, strontium, and barium by dissolving the respective oxides in hydronitric acid. They stated that all of these compounds crystallised without water of crystallisation, except those of lithium and barium, to the first of which they assign the formula $\text{LiN}_3 \cdot \text{H}_2\text{O}$, and to the second $\text{BaN}_6 \cdot \text{H}_2\text{O}$. Curtius and Rissom, in the article above quoted, state that all of these trinitrides are without water of crystallisation, and advance in proof of that statement analyses of lithium trinitride and barium trinitride that show fairly good agreement with the results calculated for the anhydrous salts. Before making their analyses, however, they dried the lithium trinitride over sulphuric acid to constant weight. They did the same with the

barium salt, but analysed also an air-dried sample of that compound, and claim that the analyses of both products showed that barium trinitride is free from water of crystallisation. Dennis and Benedict had no intention of giving the impression that they considered it impossible to dehydrate the trinitrides of lithium and barium by long-continued drying over concentrated sulphuric acid, nor did they suppose that analyses of salts dried in this manner would give a correct idea of the composition of those compounds as they separate from solution. To make sure, however, that water of crystallisation is present in the two salts in question, Mr. J. H. Pettit prepared, in this laboratory, fresh portions of the trinitrides of barium and lithium, drying these samples in air between sheets of filter-paper, and then over night in a desiccator containing calcium chloride. His analyses gave the following results:—

TABLE IV.

I	Calculated for.		Found.	
	LiN_3	$\text{LiN}_3 \cdot \text{H}_2\text{O}$	I	II
	Percent	Percent	Percent	Percent
	44.29	40.40	40.82	40.88
	BaN_6	$\text{BaN}_6 \cdot \text{H}_2\text{O}$	I	II
	Percent	Percent	Percent	Percent
Ba. .	66.96	57.32	57.16	57.31

To ascertain whether the air-dried, hydrated barium trinitride would lose water of crystallisation on standing over sulphuric acid, 0.2429 gm. of the air-dried salt was allowed to stand for two months in a desiccator containing sulphuric acid. The amount of water contained in the above-mentioned weight of $\text{BaN}_6 \cdot \text{H}_2\text{O}$ is 0.0184 gm. The salt lost, on standing, over the sulphuric acid 0.0182.

The above analyses confirm the statement of Dennis and Benedict that lithium trinitride and barium trinitride, as crystallised from aqueous solutions, contain each one molecule of water of crystallisation.

Silver Trinitride.—Curtius (*Ber.*, 1890., xxiii., 3023) states that silver trinitride is insoluble in water and dilute acids. Both of these statements are incorrect. As pointed out by Dennis (*Journ. Am. Chem. Soc.*, 1896, xviii., 947), silver trinitride is soluble in dilute, hot nitric acid, and recent experiments by the authors have shown that the compound is also somewhat soluble in boiling water (about 0.1 gm. in 1 litre of water), and that it crystallises in minute needles from this solution. This crystalline form of silver trinitride has already been mentioned by Angeli (*Atti. R. Accad. dei Lincei Roma*, 1893, [5], ii., 1., 569).

(To be continued.)

NOTE ON THE ELECTROLYTIC PREPARATION OF TITANOUS SULPHATE.

By W. H. EVANS, B.Sc.

DESPITE the important applications of the titanous salts during the last few years, and the fact that they are now prepared technically by electrolysis,* no data have been published to show the influence upon the yield of varying the conditions of working. It seemed, therefore, of some interest to investigate the effect of the current density, concentration of solution, and temperature at which the electrolysis is carried out, upon the course of this electrolytic reduction. Up to the present only titanium sulphate has been dealt with.

In the earlier work the solutions were electrolysed in a beaker, with a porous pot to separate the anode from cathode chambers, but it was soon found that the solution of titanous sulphate, despite the very powerful reducing properties of this compound, is quite stable, and that very

* Howard Spence and P. Spence, *and* S. J. Fox, *Patents* No. 15,196 and 15,630 of 1902.

good yields could be obtained without the use of any diaphragm. Provided the current density at the anode is kept fairly high, the oxygen is evolved without effecting any marked oxidation of the titanous salt. This, of course, considerably simplifies the preparation, and in all the later work the electrolysis was carried out in a beaker or vat in which the electrodes were suspended at some distance apart. Moreover, the P.D. required is much lower owing to the smaller resistance of the cell (2·5 to 3·5 volts instead of 4 to 5 volts).

Effect of Varying the Current Density.—With a solution containing 40·8 grms. titanium sulphate per litre in a beaker containing 400 c.c., with a current of 3·5 ampères (=14 ampères per 100 sq. cms.), the yield at 20 minutes after starting was 31 per cent, after 33 minutes 22 per cent.

With the same solution, but with only 1·7 ampères (=6·8 ampères per 100 sq. cms.), the yield at corresponding times was 62 and 50 per cent respectively. That the yield falls rapidly with increase of current density was fully borne out by the results of a series of preliminary experiments, using a porous pot.

Influence of Temperature.—It was found that by raising the temperature at which electrolysis was carried out the yield could be considerably increased. The comparative experiments were arranged by connecting two electrolytic cells containing the same solutions (81·6 grms. $\text{Ti}(\text{SO}_4)_2$ per litre) in series. One cell was kept at 70° C., the other as near 0° C. as possible. At the higher temperature, with a current density of 4·5 ampères per 100 sq. cms., the yield could be kept above 70 per cent until quite half of the titanium sulphate had been reduced.

In the cold solution, on the other hand, the yield was only about 45 per cent of the theoretical; the difference in the two cases was very clearly seen in the fact that there was no visible evolution of hydrogen at the cathode in the hot solution, whereas in the cold a considerable amount of hydrogen was given off.

Effect of Concentration.—In the preliminary experiments, using a porous pot to separate the anode from the cathode, the influence of concentration within the limits of 85 to 17 grms. of titanium sulphate per litre was very evident, for with a current density of about 7 ampères per 100 sq. cms., and a temperature of 15° to 17° C., the yields were as follows:—

1. Solution containing 85 grms. $\text{Ti}(\text{SO}_4)_2$ per litre, 75 per cent.
2. Solution containing 42·5 grms. $\text{Ti}(\text{SO}_4)_2$ per litre, 33 per cent.
3. Solution containing 17 grms. $\text{Ti}(\text{SO}_4)_2$ per litre, 2·2 per cent of the theoretical for the current used.

In comparative experiments in which platinum electrodes were substituted for those of lead no very great difference in yield could be observed, possibly with lead better results were obtained.

The estimation of the amount of titanous salt obtained was carried out by titrating a small quantity of the solution from the cell with standard permanganate, after warming to 60° or 70° C.

In all the experiments the cathode solution was well stirred, either by a mechanical stirrer or by passing a current of some inert gas.—*Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, xlix., Part I.

Royal Institution.—On Tuesday next (December 27), at 3 o'clock, Mr. Henry Cunyngame will deliver the first of a Christmas course of six lectures, adapted to a juvenile auditory, on "Ancient and Modern Methods of Measuring Time" (Experimentally Illustrated). The following are the subjects for the lectures:—Ancient Sundials and Clocks, the Discoveries of Galileo, the Pendulum and Balance-wheel, How a Clock is Made, More about Clocks and Watches, Quick Time Measurements of the Speed of Cannon-balls and of Light.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1904.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, December 9th, 1904.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 212 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 212 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford during the month has been below the average; the actual amount recorded was 1·59 inches. The average for November is 2·30 inches, leaving a deficit of 0·71 inch, which, if added to the previous deficit of 1·61 inches, gives a total deficit for the year of 2·32 inches, or to per cent on the thirty-five years' average.

Our bacteriological examinations of 378 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 395 others from special wells, standpipes, &c., making 773 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	200
New River, filtered (mean of 77 samples) ..	8
Thames, unfiltered (mean of 26 samples) ..	2407
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 197 samples) ..	18
Ditto ditto highest	189
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	236
River Lea, from the East London District clear- water wells (mean of 24 samples) ..	16

Of the 298 daily samples taken from the general filter wells of the Metropolitan Water Board, twenty-three samples, or 7·7 per cent, were sterile. Eight samples, or 2·6 per cent, contained more than 100 microbes, and of these four samples contained more than 150 microbes per c.c. The eight excess samples contained an average of 140 microbes per c.c. In October four excess samples contained an average of 130 microbes per c.c.

Considering the unavoidable fluctuations which will inevitably take place in a water supply derived primarily from two large rivers, the quality of the water distributed to London during the month of November must be characterised as excellent.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

(Ordinary Meeting, December 10th, 1901.)

Dr. R. T. GLAZIER, F.R.S., President, in the Chair.

Prof. S. P. THOMPSON read a paper "On a Rapid Method of Approximating Harmonic Degrees."

For the study of alternating electric currents and for several other applications, harmonic analysis is simplified by the consideration that all the even terms in the Fourier expansion are absent. In this case the second half-period is similar to the first half-period, but with the ordinates of the corresponding angles reversed in sign. Given a complicated harmonic curve containing constituents of the odd orders only, the zero-line can always be drawn so that the constant term vanishes from the Fourier series, the mean ordinate being zero; and it is then always possible to choose as origin a point for which the ordinates at 0° and 180° are zero.

The paper gives a *résumé* of the various methods which have been employed for harmonic analysis by reduction from simultaneous equations, graphical means, and by harmonic analysers. The method adopted by the author is a simplification of a general method of analysis published by Prof. Runge. The half-period of the wave is divided into $2m$ equal parts giving $2m-1$ equidistant ordinates. These ordinates are then put together in pairs, so that there then may be found the sum and difference of the ordinate of any angle and the ordinate of its supplement. The sum will contain sine-components only, and the difference cosine-components only. The sums are used for getting out the coefficients of sine-terms, and the differences for getting out those of the cosine-terms. A further grouping is employed for the higher harmonics of those orders for which the ordinal number is a factor of the number of division m , by means of which a saving of multiplication is effected. The numbers assembled and grouped are arranged in a convenient schedule, each number as it is entered being multiplied by the sine of the angle set over against it. The coefficients of the n th order are given by the integrals—

$$A_n = \frac{2}{T} \int_0^T y \cdot \sin npt \cdot dt \text{ and } B_n = \frac{2}{T} \int_0^T y \cdot \cos npt \cdot dt.$$

Hence it is necessary to integrate and take twice the means. The integration becomes a mere summation of the products made during the preceding processes. But since in the case where, say, 12 ordinates are taken, the 11th coefficient would be got out by multiplying by the same sines as would yield the 1st coefficient, only with alternate + and - signs prefixed, the addition for both the 1st and the 11th harmonic may be effected by finding separately the sums of the alternate product-numbers, which are therefore set down alternately in two columns. The totals of the first column and of the second column are therefore made separately. The sum of them gives the "integral" for the 1st harmonic, the difference between them gives the "integral" for the 11th harmonic, and so forth. The labour of the process varies approximately as the cube of the number of ordinates taken. Using 18 ordinates the time taken to complete the whole analysis is about seventy minutes; for 12 ordinates it is about twenty-five minutes, and for 6 ordinates under two minutes.

Dr. J. A. FLEMING said that he had found by experience that most alternating-current curves of current or E.M.F. which occurred in connection with transformer working, could be quite nearly represented by a simple sine curve added to the two first odd harmonics having wave-lengths one-third and one-fifth of the primary. Hence the analysis of any such curve as the magnetising curve of a current-transformer resolved itself simply into the determination of the amplitude and phase-difference of these three con-

stituents. They were indebted to Prof. Thompson for bringing before them such a simple arithmetical process of resolution, which reduced the performance of the Fourier analysis of simple periodic curves to little more than mere arithmetic, even more simple than Horner's process for obtaining the arithmetic real roots of an equation of the n th degree. In addition to the analysis of a single periodic curve, it was useful sometimes to be able to perform the synthesis rapidly, and Dr. Fleming exhibited and described a simple form of instrument which he had designed for effecting this. The instrument was constructed to draw the compound polar curve corresponding to a fundamental and the first two odd harmonics, and a diagram was exhibited showing the corresponding wave-form for one setting, which was extremely similar to the no-load magnetising current of a transformer. Diagrams were also exhibited showing how nearly the magnetising current of a transformer could be represented in wave-form by the use of such an apparatus. He said that the representation of alternating-current curves by polar diagrams had particular advantages, and it was much to be wished that some enterprising stationer would provide polar ruled paper for plotting polar diagrams, analogous to squared paper.

Mr. J. HARRISON pointed out that the author's system of harmonic analysis could very readily be performed entirely by graphical methods, and moreover, subject to certain restrictions, could be employed to find even terms as well as odd ones. He exhibited a graphical schedule for a particular case and demonstrated its use.

A paper on "A High Frequency Alternator" was read by Mr. W. DUBBEL.

The author described and showed in action a high-frequency alternator which he had constructed in 1900 for some experiments on the resistance of the electric arc, and with which frequencies up to 120,000 per second had been obtained. The alternator consists of an inductor, built up out of ferrotype plate, having V-shaped notches cut in its edge so as to have flat-topped teeth. Surrounding the inductor is a laminated ring having two inwardly projecting poles, the clearance between these and the teeth of the inductor, which formed the air-gap, being less than 0.1 m.m. The ring is wound so that a direct current flowing round the winding tends to produce lines of force from one pole to the other through the inductor. The number of lines of force varies from a maximum when the teeth of the inductor are opposite the poles, to a minimum when the poles are in front of the spaces. This variation in the total number of lines of force produces alternating E.M.F.'s in any winding either on the pole-pieces or on the ring itself; the movement of the inductor through the distance between two consecutive teeth producing one complete period. One winding on the ring could serve to carry both the direct current which magnetises the ring and the alternating current produced. In practice, owing to the great importance of any self-induction in the alternate-current circuit, it was found advisable at high frequencies to use separate windings for the two currents. At the highest frequencies the best results were obtained with coils having a few turns of wire fixed right on the tips of the poles. The alternator is driven by means of a figure-of-8 belt driven from two phosphor-bronze discs. Each of these discs is belted to a double-grooved pulley fixed on the shaft of a direct-current driving motor. With this method of drive the inductor was run for several months at speeds between 30,000 and 40,000 revs. per minute, and the spindle of the inductor alone could be easily run at 60,000 revs. per minute. Using inductors having 30, 60, 90, and 204 teeth, the author obtains small alternating currents having frequencies from a few hundred periods per second up to 120,000 per second. An illustration will perhaps convey some idea of how high a frequency of 120,000 per second really is. In plotting curves for ordinary frequencies of 50 to 100 per second, a scale often adopted is 10 inches for 100. If it were attempted to plot a curve up to 120,000 per second to

OBITUARY.

SIR LOWTHIAN BELL.

this scale, the curve paper would require to be 120,000 inches, or nearly *one-fifth of a mile long*. Many difficulties were encountered with the centrifugal forces on the driving-belt, and the author finally obtained the best results with a spliced cotton cord. Working drawings of the alternator, characteristic curves, and its wave-form are given in the paper. During the construction of the alternator bicycle wheels were used to drive it, and curves are given showing the very large power taken to drive these wheels, owing to air friction. A table is given of all the high-frequency alternators which have come to the author's knowledge, and he would be glad to receive any missing data or data of other machines to include in the table before it is finally printed.

Dr. J. A. FLEMING said he had felt surprised on hearing about Mr. Duddell's alternator that he had been able to reach any such frequency as 120,000 $\sim$ per second. It spoke highly of the excellent mechanical means employed. On the other hand, as far as its use in wireless telegraphy was concerned, it was no use to speak of a machine even if it gave this frequency, corresponding to a wave 14 miles in length, if the output of the machine were only a few watts. If it were 150 H.P. it might be different. The difficulty with most high-frequency alternators was the magnetic leakage. Dr. Fleming then described some of the devices adopted by Tesla for obviating this defect. Many of the high-frequency alternators made had their power overestimated. Hitherto the frequency reached had been only about 10,000 $\sim$ per second. A machine of this last frequency would be no particular assistance in wireless telegraphy. Such machines were, however, very useful for research and demonstration purposes.

Prof. W. E. AYRTON gave an Exhibition of Experiments to show the Retardation of the Signalling Current on 3500 miles of the Pacific Cable between Vancouver and Fanning Island.

The experiments were performed upon a cable electrically equivalent to the portion of the Pacific Cable between Vancouver and Fanning Island, the product of the capacity (in mfd.) and the resistance (in ohms) being nine millions. Three dead-beat galvanometers were employed to indicate the current at the beginning, in the middle, and at the end of the cable. It was shown that upon applying an E.M.F. at one end of the cable the current at that end was enormously greater than its steady value, and that one-fifth of a second elapsed before any indications of current were shown at the far end of the cable. By that time the current at the sending end was 3.7 times its steady value, and after two-fifths of a second it had fallen to 2.3 times its steady value. In about five seconds the current became steady.

The Electrical Laboratories of the College were open to the inspection of Fellows, a special feature being an exhibition of Ayrton-Mather Galvanometers (showing the evolution of the present commercial instruments from the earliest types, constructed in the College), Universal Shunts, and Electrostatic Instruments.

Purification of Sodium Vanadate Liquors. Remarks upon the Industrial Separation of Metals by Double Decomposition.—M. Herrenschildt.—In reply to a question from the Patent Office at Berlin, as to why vanadic acid rather than any other acid was used in precipitating silica from a solution of sodium vanadate, the author states that vanadic acid is the only acid which will precipitate silica from a *dilute* solution. Moreover, if sulphuric acid, for instance, is used with a concentrated solution, both vanadic acid and silica are precipitated, and there is no separation. This method of separating metals from a solution by the addition of a compound of one of them rather than by adding a foreign substance, is in use in several manufactories, e.g., zinc is separated from copper by the addition of zinc oxide, cobalt from nickel by the addition of nickel sesquioxide, &c.—*Comptes Rendus*, cxxxix., No. 21.

WE regret to announce that the veteran ironmaster and metallurgist, Sir Isaac Lowthian Bell, died at his residence, Rounton Grange, Northallerton, on Tuesday, December 20th, within a few weeks of completing his eighty-ninth year. He was born on February 15th, 1816, at Newcastle, his father being an ironmaster, Mr. Thomas Bell, and his mother a daughter of Mr. Isaac Lowthian, of Newbigin, in Cumberland. After attending Edinburgh University and the Sorbonne, he spent some time in travel on the Continent, and then, at the age of twenty-four, entered the Walker ironworks, near Newcastle, in which his father was a partner. There he remained till 1850, when he became connected with the chemical works at Washington, in North Durham. Under his direction these became one of the most important concerns of their kind in the North of England. He greatly enlarged them, and laid down extensive plant for the manufacture of an oxychloride of lead introduced as a substitute for white lead by his father-in-law, Mr. H. L. Patinson, F.R.S., with whom he was associated in the business at Washington. There, too, was introduced, in 1860, almost the first plant in England for the manufacture of aluminium by the Deville sodium process.

Soon after the discovery of the main bed of Cleveland ironstone near Middlesbrough by John Vaughan in 1850, in conjunction with his brothers, Thomas and John, he started ironworks at Port Clarence, on the north bank of the Tees. A little more than half a century ago the site of Port Clarence was a waste of mud and marsh—in fact, the Tees then flooded ground where iron furnaces now stand. Much land in the estuary has since been reclaimed—largely by means of the "cinder balls" from the furnaces, which were used to build retaining walls—and on a portion of this were placed the iron-smelting works of Bell Brothers, among the largest in the Cleveland district. From the first they were carried on in an enterprising and economical spirit. To most people the site upon which they were erected would have seemed unpromising enough, yet in fact it had facilities for land and water carriage and possibilities of extension at very reasonable expense. The firm acquired their own ironstone mines, collieries, and limestone quarries, while they have always been prompt to adopt any improvement in process or apparatus that has seemed likely to be advantageous. For example, when it was found that economy in fuel resulted from increase in the height of blast furnaces, they re-constructed their plant, in view of that fact, and they were among the first in the Cleveland district to take advantage of the saving effected by the use of the waste gases for heating the blast. In the development of the Cleveland iron industry they thus played a very important part, and what has been the extent of that development may be judged from the fact that, whereas the district in 1850 produced less than 25,000 tons of pig-iron, at the present time Middlesbrough accounts for about one quarter of the total output of this country. Not only were they largely responsible for the surveys which revealed the position and extent of the ironstone beds, but they were active in prosecuting those technical studies by which processes have been devised enabling Cleveland ores to compete as raw material for the production of iron and steel with others possessing greater natural advantages. In regard to steel, the great trouble with those ores is the high percentage of phosphorus (1.8 to 2.0 per cent) contained in the cast-iron which they yield; yet Middlesbrough, largely as a result of experiments carried on under Sir Lowthian Bell's direction, at a cost, it is said, of between £40,000 and £50,000, produces steel rails in which this percentage is reduced to 0.07 or less. Many thousand tons of such basic steel rails have been laid on the North-Eastern Railway, of which he was a director, and the careful records kept of their behaviour convinced him that

neither in loss of weight by wear nor in the number of breakages do they give any ground for complaint. In connection with rails it is interesting to note, as an illustration of the advances made during his exceptionally long and active life, that he could remember seeing wooden rails in use on the tramroads by which coal was brought down to the river Tees. Middlesbrough steel has also been rendered available for shipbuilding purposes, and as chairman of the company he had, in 1901, the satisfaction of announcing that the product of the Clarence Works fulfilled all the requirements of Lloyd's Registry.

Sir Lowthian Bell had an intimate knowledge, both on the scientific and statistical sides, of the iron and coal deposits of the North of England. When the British Association met at Newcastle in 1863, he contributed a paper on the manufacture of iron in connection with the Northumberland and Durham coalfields, in which he calculated that the supply contained in that coalfield was just about sufficient to smelt the ironstone in the main Cleveland seam, supposing none of it to be used for any other purpose. His aptitude for statistics was also shown in other ways. In 1870 he wrote a paper bristling with facts and figures, on the sanitary condition of Newcastle, and more recently he compiled an elaborate account of the iron trade of the United Kingdom, compared with that of the other chief iron-making countries. On the chemistry of iron he was a very high—if not the highest—authority. The establishment of a chemical laboratory in connection with the Clarence works shows how fully he realised the importance of the scientific study of industrial processes, and his own researches on the chemistry of iron and steel, some of which have been translated into French and German, have become classic. Many of the most important of these appeared first in the form of papers read before the Iron and Steel Institute, and a number of them were subsequently collected and published in a thick volume entitled "The Chemical Phenomena of Iron Smelting." Sir Lowthian was also the author of a book on the "Principles of Iron and Steel Manufacture," as well as of many papers contributed to other scientific societies.

In the Iron and Steel Institute he took a great interest. One of its original founders in 1869, he filled the office of president from 1873 to 1875, and in 1874 became the first recipient of the gold medal instituted by Sir Henry Bessemer the year before. Among the learned societies he was a member of the Civil Engineers and of the Chemical Society, and a past president of the Institution of Mechanical Engineers. In a presidential address to the Institution of Junior Engineers in 1900, he gave a short account of the development of the iron trade, and after claiming that Great Britain had been almost the sole author of the improvements that had raised the industry to its present position, declined to admit that our reduced production was due to any inferiority in methods of manufacture. In 1874, the Royal Society made him one of their number, and he had the distinction of being elected an honorary member of the American Philosophical Institution. In the municipal affairs of Newcastle he took a prominent part, having been a member of the Town Council for many years, and having held the mayoralty twice; and he was a director of the North-Eastern Railway. He was a J.P. and D.L. for the county of Durham, and served as sheriff in 1884. He made several attempts to enter Parliament, but was somewhat unfortunate. He contested North Durham in 1868, but was defeated. Six years afterwards he stood again for the same constituency, and was returned at the head of the poll. The election, however, was held void on the ground that intimidation had been practised at certain places, and at the new election thus rendered necessary Sir Lowthian Bell was at the bottom of the poll. In the following year (1875) success attended his efforts at Hartlepool, for which he sat in the Liberal interest till 1880. The honour of a baronetcy was conferred on him in 1885, and in 1893 he received the Degree of LL.D. from Edinburgh University.

Sir Lowthian married, in 1842, Margaret, the second daughter of Mr. H. L. Pattinson, by whom he had six children. The title goes to Mr. Hugh Bell, born in 1844, whose wife, daughter of the late Sir Joseph Olliffe, M.D., is well known as the writer of several novels and of a number of plays, both in English and French, some of which have been produced in London, including *L'Indécis*, produced by Coquelin at the Royalty in 1887. One of Sir Lowthian's daughters is the present Lady Stanley of Alderley.—*The Times*.

MISCELLANEOUS.

Double Cyanides of Mercury.—Hermann Grossmann and Peter Von der Forst.—Analysis of the potassium double cyanide gives the formula $K_2Hg(CN)_4$. In the sodium salt the double molecule, $Na_2Hg(CN)_6$, exists, as is shown by determinations of the lowering of the freezing-point of water and conductivity determinations. Possibly the sodium salt in solution splits up into $Na_2Hg(CN)_4$ and $Hg(CN)_2$, the latter being a non-electrolyte. No solid ammonium compound is known. The barium and strontium salts belong to the same type as the potassium salt, but are hydrated and unstable in air. Both compounds crystallise in colourless prismatic needles. The calcium salt exists in two forms, having the formulae $CaHg(CN)_6 \cdot 3H_2O$ and $Ca_2Hg_3(CN)_{10} \cdot 6H_2O$ respectively. The magnesium salt belongs to the same type as the latter of these.—*Berichte*, xxxviii., No. 15.

Withdrawal of Oxygen by Platinum.—E. Goldstein.—It has been observed that in Geissler tubes the substance of the platinum cathode is gradually removed to the glass wall, and there forms shining mirrors, which up to a certain thickness are translucent. Mirrors which show the colours of the pure metal (green for gold, blue for silver, greyish black for platinum) are only obtained in hydrogen. If the gas contains oxygen the colours are impure, and as the amount of oxygen increases the colours approach nearer to those of the oxides of the metals. The author has now observed that the oxygen is absorbed very quickly if the cathode is ignited to a yellowish white heat. For pure oxygen platinum wires about 0.4 m.m. thick by a free length of about 1 c.m. are used. Such wires become intensely hot on exhaustion of the tubes, even with medium sized inductors, if a powerful primary current is applied. Thus, if a cylindrical tube of 2 to 3 c.m. width and a capacity of 50 to 100 c.c. is filled with oxygen of the usual density for Geissler tubes, if when the discharge passes the cathode glows strongly the oxygen is absorbed in one to two minutes. If the tube is filled with rarefied dry air the absorption of oxygen occurs in a still shorter time. The wires are then somewhat thinner; i.e., about 0.25 m.m. thick. The complete elimination of oxygen in any mixture of nitrogen and oxygen can be demonstrated by the fact that the discharge appears yellowish gold instead of red in nitrogen which is free from oxygen. The avidity with which platinum attracts oxygen can be used to free rarefied gases from traces of oxygen. If the pressure of the gas rises above a certain limit, the intensity of discharge obtainable for a given inductor will no longer suffice to bring the cathode to intense heat. In such cases the cathode wire (then somewhat longer) has both ends melted into the glass wall, so that it can be connected by means of external hooks with an accumulator of three cells. By means of a resistance regulator an additional current can be passed through the wire which will cause bright glowing. The method can thus be used for all densities in which a perceptible destruction of the cathode occurs, and hence there is an essential connection between the two phenomena. The energetic oxidation of the platinum is also connected with the conversion of oxygen into ozone when the discharge passes in Geissler tubes.—*Berichte*, xxxviii., No. 15.

An Improved Form of Crucible Lid.—In most school practice, an important type of experiment is the one where copper is converted into cupric oxide by means of nitric acid. This is usually done in a porcelain crucible, but it has been found that anything like uniform or even approximately accurate results have been impossible, even with the most careful workers, owing to the loss of liquid during effervescence and evaporation. The form of crucible lid is the main cause of these inaccurate results. Any liquid coming on the lid during effervescence or evaporation is led to the side, and then generally finds its way down the outside of the crucible. The improved lid has been



designed to obviate this. It is made slightly convex to the crucible, so that any liquid splashing on the lid is led back to the centre and drops back into the crucible. When lifting the lid during the experiment, it is of course necessary to lift it horizontally. The results given below show the values obtained by the use of the improved lid. They were obtained by a first-year class weighing only to the second place of decimals. The results obtained with the ordinary lids is also given. The form of the lid does not in any way interfere with its usefulness for other experiments.

Weight of Oxygen combined with 1 Grm. of Copper.

With ordinary lid		With the improved lids	
0.22 grm.	0.19 grm.	0.27 grm.	0.25 grm.
0.21 "	0.19 "	0.26 "	0.24 "
0.20 "	0.18 "	0.25 "	0.24 "
0.20 "	0.17 "	0.25 "	0.24 "
0.19 "	0.16 "	0.25 "	0.23 "
0.19 "	0.12 "	0.25 "	0.22 "

These improved crucible lids are supplied by John J. Griffin and Sons, Ltd., 20-26, Sardinia Street, London, W.C.

MEETINGS FOR THE WEEK.

TUESDAY, 27th
THURSDAY, 29th
SATURDAY, 31st

Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Ancient and Modern Methods of Measuring Time" (Experimentally Illustrated), by Henry Cunyngame, C.B., &c.

ABSOLUTE ALCOHOL,

FREE FROM DUTY,

FOR SCIENTIFIC AND RESEARCH WORK IN LABORATORIES

To be obtained from

HUGO LORENZ,

7-8, Idol Lane, Great Tower St., London, E.C.,

Licensed Trader in Alcohol and Spirits of Wine.

Stock kept in suitable packages ready for immediate use

PLATINUM UTENSILS, SCRAP. LAMP-ENDS, &c.,

Purchased at highest prices by—
DERBY & CO., LTD., 44, CLERKENWELL ROAD, LONDON.
N.B.—Platinum Sold.

REDRUTH

SCHOOL OF MINES.

School Re-opens Jan. 4th,
1905.

Syllabus on application to—

THE REGISTRAR.

MR. EDWARD ARNOLD'S NEW BOOKS.

THE CHEMICAL SYNTHESIS OF VITAL PRODUCTS

AND THE
INTER-RELATIONS BETWEEN ORGANIC COMPOUNDS

BY
R. MELDOLA, F.R.S., V.P.C.S., F.I.C., &c.,
Professor of Chemistry in the City and Guilds of London
Technical College, Finsbury.
Super Royal 8vo. 21s. net.

THE BECQUEREL RAYS AND THE PROPERTIES OF RADIUM

By the Hon. R. J. STRUTT,
Fellow of Trinity College, Cambridge.
Demy 8vo. With Diagrams. 8s. 6d. net.

AN INTRODUCTION TO THE THEORY OF OPTICS.

By ARTHUR SCHUSTER, Ph.D., Sc.D., F.R.S.,
Professor of Physics at the University of Manchester.
Demy 8vo. With numerous Diagrams. 15s. net.

THE ELECTRIC FURNACE.

By HENRI MOISSAN,
Professor of Chemistry at the Sorbonne.
Translated by A. T. de MOUILPIED, M.Sc., Ph.D.
Demy 8vo. With numerous Illustrations. 10s. 6d. net.
London: EDWARD ARNOLD, 41 & 43, Maddox St., W.

RECTIFIED SPIRIT

(SPIRITS OF WINE).

B.P. and higher strengths. Duty paid; or
Duty Free under Finance Act 1902.

METHYLATED SPIRIT

Special Quotations to large
Institutions.

BOORD & SON,

DISTILLERS SINCE 1730,

115-121 Tooley Street,
LONDON, S.E.

ACETONE,

Chemically and Tech. pure.

METHYL-SPIRIT.

WOOD

NAPHTHA.

METHYLENE, Type Regie.

ACETON OIL.

&c.

Chemische Fabrik Eidelstedt,

John Oswaldowski, Altona E.

THE CHEMICAL NEWS.

VOL. XC., No. 2353.

SERIAL ORDER OF THE RARE EARTHS.

By G. URBAIN and H. LACOMBE

ELEMENTS belong to the same family when their compounds of the same type are isomorphous and when they present, as a whole, the same chemical functions.

Generally speaking, such elements co-exist in their ores. In the case of the rare earths, in particular, the presence of one of them is scarcely detected without at the same time detecting the presence of all the others.

Two elements are the more closely related in proportion to the closeness of their isomorphic relations. Thus, cesium is more nearly allied to rubidium than to potassium. Without the possibility of formulating, in the present stage of our knowledge, a quite accurate law on this subject, it is probable that the elements of one family constitute the successive terms of a series, in the mathematical sense of the word. We will designate the logical order in which the elements of one family might be arranged by the name of "Serial Order." Between two consecutive terms of the serial order, the isomorphism is more perfect than between any other two terms of the family.

From one term of the order to another there is a gradual modification of the chemical and physical properties, and these properties might, for the most part, be represented by functions really continuous with regard to limiting laws relative to isomorphous mixtures of which the properties are approximately the mean of the properties of their constituents.

In particular, two consecutive terms of the serial order are those of which the different isomorphous compounds are the most difficult to separate. It is this characteristic which, in a complex series such as that of the rare earths, admits of determining the serial order.

The solubility appears thus to be the fundamental characteristic which serves as a guide in the serialisation.

Just as a pencil of rays of different refrangibility can be dispersed by a prism, which classes them in a constant order whatever be the nature of the prism, so, in the same way, a mixture of isomorphous elements may be said to be "dispersed" by fractional crystallisation, which thus classifies the different terms in the order, generally constant, of the solubility of their salts, whatever be the nature of the salt chosen.

M. Locke has established a law of this order in connection with the alums and double sulphates of the magnesium series.

If, in a general way, the facts were presented with a like simplicity, there would exist a "law of the serial order," which would have long been enunciated, and which would play a useful part in chemistry. But, as a matter of fact, the order of the solubilities apparently differs for the types of different salts, and all that we can affirm is that very frequent coincidences exist.

These coincidences occur especially in the different terms of a natural family; they are less frequent in connection with the different terms of an isomorphous series which do not necessarily belong to the same natural family. Thus cerium, rubidium, potassium, and thallium form a group of isomorphous elements, but thallium cannot be considered as belonging to the natural family of the metals of the alkalis.

It is very remarkable that the group of the rare earths, the different terms of which are still so little known, should be the best studied from the special point of view with which we are occupied. Of all the natural families this contains

the greatest number of elements, the number being almost a quarter of the number of all the elements actually known.

The serialisation of the rare earths affords the highest interest, because there is ground for hoping that the relations attaching to the different terms of this series may be extended to other families of elements, and that finally there may be deduced from these laws a system of classification of the elements more coherent than that of Mendeleeff.

The total work on the rare earths permits of classing in the following order the best characterised terms of the series:—Lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, γ-terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium.

We do not make scandium appear in this list. We found it impossible to follow it in our fractionations, and we think our earths did not contain it. In addition to this, the little that is known about it leads to no analysis. It has been shown that in the group of rare earths, properly so called, the earths of low equivalent are the strong bases, and the earths of high equivalent are the weak bases.

The equivalent of scandium is lower than that of any one of the rare earths. Also the double potassium sulphate of scandium is insoluble in potassium sulphate, and this characteristic would allow of its being placed among the cerium earths.

If we consider that from lanthanum ($La = 138$) to terbium ($Tb > 163$) the atomic weights are constantly increasing, we feel some hesitation in inserting scandium ($Sc = 44$) among these elements. We think, therefore, that scandium belongs to some other series of elements, being allied either to thorium and uranium or to glucinum.

In order to justify the preceding serialisation of the rare earths, it is enough to recall the fact that most of the methods of separation allow of their being obtained successively in this order. This is the case with the double ammoniacal nitrates (Von Welsbach); also with the double nitrates of the magnesium series (Demarçay); also with the double alkaline sulphates (Lecoq de Boisbaudran); also the ethyl sulphates of the yttrium earths (G. Urbain).

The study of the other salts is still too incomplete for one to be able to affirm that the law is absolutely general; but we know of no fact, nor have we observed one, which formally contradicts it.

A certain number of cases exist in which it seems to break down, viz., when any one of the intermediate terms of the series appears at the head of the fractionations, as is the case with gadolinium when the simple nitrates with five molecules of water are fractionated (Demarçay).

It can be shown that this anomaly is only apparent. Let us fractionate thus the earths containing only lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium. We shall obtain successively the nitrates in the inverse order to that in which we have just enumerated them.

The experiment was not done in this manner; but in the presence of yttrium earths one can successively observe their presence in this order from the beginning to the end of the fractionations.

The yttrium earths separate as simple nitrates in their normal order.

One of us made a great number of fractionations of these nitrates. They will be described in detail later on.

Thus, in this case, it is the existence in the series of a minimum solubility which seems to falsify the theory of the serial order, but it is obvious that this anomaly is only apparent. Several types of salts present similar minima. Thus we have proved the existence of a minimum corresponding to didymium in the series of the ethyl sulphates. Others exist for the acetates, oxalates, &c.

It would suffice that certain salts present at once a maximum or a minimum in the series in order to make the confusion of the solubilities appear complete, and to invalidate, to all appearance, the theory of the serial order.

These kinds of redoubling of the series upon itself may

be compared to the cases of anomalous dispersion, and to the cases of anomalous dilatation of certain liquids—such as water. The existence of the maximum density of water at 4° does not invalidate the general law of the expansion of liquids; the existence of anomalous solubilities should not similarly invalidate the law of the serial order. It is very evident, however, that such a law could only appear to advantage in a series such as that of the rare earths, the terms of which are very numerous.

In the families of ordinary elements which contain a very restricted number of terms, the preceding theory loses much of its interest.

The physico-chemical properties of the rare earths follow the law of the serial order very well.

From what is known of fractionations based on differences of basicity, it is manifest that any earth whatever presents, in general, a basicity intermediate between that of the term which precedes it and of the term which follows it in the serial order. Lanthanum oxide—first term of the series—is a very strong base. The basicity diminishes first with the terms following. It seems to pass through a minimum with the earths of terbium. It increases finally to a maximum with yttrium, then rapidly decreases in passing through erbium, thulium, and finally ytterbium—last term of the series—the oxide of which is a feeble base, the weakest of the group.

The atomic weights follow approximately, in the serial order, a law inverse to the basicity, the maximum corresponding to the terbium earths and the minimum to yttrium.

In the present state of our knowledge of the rare earths, the preceding theory can have no absolutely scientific accuracy; but we thought it our duty to expound it in this preliminary article, because it has been a remarkably sure guide to us in our researches, alone or together, on the separation of the rare earths for nearly ten years.

THE DETERMINATION OF CHROMIUM IN STEEL.

By F. IBBOTSON, B.Sc., and R. HOWDEN, B.Sc.

The usual volumetric methods for the determination of chromium in steel consist in the oxidation to chromic acid by means of a strong solution of potassium permanganate. This is added until, in the boiling solution, a permanent precipitate of manganese dioxide is obtained; the latter is then either filtered off or dissolved in hydrochloric acid. In the one case, the precipitate obstinately retains a small amount of chromium, which may, however, be washed out with sodium hydrate, and in the other case the expulsion of the chlorine is often troublesome. These inconveniences may be eliminated by using ammonium persulphate as the oxidant. Marshall made the observation that chromium salts are oxidised by persulphates alone, and found that the oxidation was accelerated by the addition of a silver salt (CHEMICAL NEWS, lxxxiii., 76), but the application of this to the determination of chromium in steel is attended with some difficulties, which we believe have stood in the way of the general acceptance of persulphates as suitable oxidising agents for the purpose.

When ammonium persulphate is added to a nitric acid solution of a steel, with or without the addition of a small quantity of silver nitrate, the manganese and chromium are speedily converted on warming to permanganic and chromic acids respectively. The oxidation is accompanied by a vigorous evolution of gas, due to the decomposition of the excess of persulphate. If the solution be boiled to effect complete decomposition, small amounts of the chromic and permanganic acids appear to be reduced again, the amounts depending, we think, to some extent on the degree of acidity of the solution. This reduction occasioned some trouble at first, but by operating in the manner described below, good results are obtained in much less time than the ordinary volumetric methods consume.

I. Steels Soluble in Nitric Acid (Specific Gravity 1.20).

The sample is dissolved in as small an amount of the acid as possible, and nitrous fumes expelled. After copious dilution, 2 or 3 grms. of solid ammonium persulphate are added together with a centigram. or so of silver nitrate, the addition of which is, however, unnecessary, provided that the solution is nearly neutral. The solution is heated until the evolution of gas commences, and allowed to stand at this temperature for a few minutes until the chromium and manganese are completely oxidised. When the amount of the latter metal is large, the oxidation to permanganate is quickly followed by a precipitation as dioxide, which must be filtered off, but in most cases there is no such precipitation. The solution is cooled, and a large excess of ammonium acetate added, after which sufficient lead acetate solution is added to precipitate the chromium as lead chromate. The precipitate is filtered through ignited asbestos, and after washing well with water containing a small quantity of pure ammonium acetate, is dissolved from the filter with nitric acid, sp. gr. 1.20. The solution is diluted freely, an excess of ferrous sulphate solution added, and the estimation completed by the use of N/20 potassium permanganate solution.

If a large excess of ammonium acetate is used, the lead chromate obtained is free from sulphate, and the nitric acid solution of the lead chromate readily lends itself to the gravimetric determination of either or both of the metals it contains.

Our experience of the process shows that the solution must not be too acid when the oxidation is being carried on. If large amounts of acid are present the oxidation fails, and the acid must be partially neutralised. In nearly neutral solutions complete oxidation can be effected in five minutes.

II. Steels not Soluble in Nitric Acid (Specific Gravity 1.20).

Steels containing large quantities of tungsten as well as chromium cannot be completely decomposed by nitric acid alone. To this class of material belong the modern high-speed cutting tool steels, which contain a trace only of manganese, and in many cases none at all. They are easily assayed for chromium in less than an hour's time by the following simple procedure:—

0.5 gm. of the drillings are treated with 10 c.c. dilute sulphuric acid (1:4), and the liquid briskly boiled to break up the sample. When decomposition is nearly complete, 2 c.c. of nitric acid (1:4) are added, nitrous fumes expelled, and luke-warm water added up to about 100 c.c. To this mixture, containing much of the tungsten as precipitated oxide, 20 c.c. of nitric acid (1:20), and 20 c.c. of silver nitrate solution (2 grms. per litre) are added, and then 2 or 3 grms. of ammonium persulphate. The mixture is then heated, and when the evolution of gas commences, the flask is vigorously shaken. The heating is continued with frequent shaking until the expulsion of gas is complete. It is then permissible to heat to boiling, and maintain in ebullition for a few seconds only. The liquid is then cooled, diluted, an excess of ferrous sulphate added, and the estimation completed as before by means of a standard solution of potassium permanganate.

The separated tungstic oxide does not seriously obscure the end of the reaction, but it can be removed by filtration if thought necessary. The removal of the silver at the same time by the addition of a few drops of hydrochloric acid leaves a filtrate ready for titration by means of ferrous solution and standard bichromate. Appended are three results from steels previously assayed by methods described by Brearley and one of us elsewhere.

Persulphate.			
A		5.86	5.87 per cent chromium
B		4.67	4.68 " "
C		2.90	2.95 " "

Sample C contained a small amount of manganese, which is included in the chromium result.

Rich chromiferous ferrotungstens can be just as readily assayed after opening out somewhat differently. These alloys are amenable to the attack of hydrofluoric and nitric acids, and when decomposition has been effected, an evaporation with the addition of a few drops of sulphuric acid provides a residue ready for the assay. An alloy, for example, containing more than 30 per cent of tungsten and 11.34 per cent of chromium yielded 11.35 per cent by this method, 0.25 grm. of the crushed sample being used.

The Chemical Department,
University College, Sheffield

THE ELECTROLYSIS OF CYANIDES.

By ANDRÉ BROCHET and JOSEPH PETIT.

In a previous paper (*Bull. Soc. Chim.*, [3], 1904, vol. xxxi., p. 359) we showed that copper, zinc, and nickel dissolve in cyanide of potassium when we use them as electrodes in an alternating current circuit (frequency 42).

Iron and platinum behave in an identical manner, but contrary to the above mentioned metals they do not act, or at least not sensibly, on solutions of cyanide of potassium even when they are used as an anode. Thus it seemed to us to be indispensable to review and complete the work that has been already done on this subject.

Action of Iron on Cyanide of Potassium.—Classic works state that iron dissolves in cyanide of potassium. This reaction is absolutely insignificant; iron in the form of strips, nails, pianoforte wires, &c., placed in a hot or cold solution of cyanide of potassium at 4 grm.-molecules per litre, gives off an extremely small quantity of hydrogen, and after a certain time we are able to detect the presence of traces of ferrocyanide of potassium, thanks to the great sensitiveness of its reactions.

If the iron is placed in contact with a strip of platinum, the gas then produced on this strip becomes a little more evident. The reaction is not much more distinct with pyrophoric iron.

Electrolysis of Cyanide of Potassium.—In a paper on the oxidation of chloride of potassium under the influence of electrolysis, Kolb (*Ann. der Chemie und Physik.*, 1847, vol. xiv., p. 236) stated that cyanide of potassium was transformed into cyanate. This assertion has never been confirmed. On the other hand, Schlagdenhauffen (*Journ. de Ph. et de Ch.*, [3], 1863, vol. xlv., p. 100) and Luckow (*Dingl. Polyt. Journ.*, vol. ccxxxix., p. 805) have shown that there was nothing formed but potash, ammonia, and carbonic acid. Further, the formation of cyanate is very unlikely on account of its instability in aqueous solution.

As we have already stated, the platinum electrodes are not attacked.

Gore observed that iron used as an anode dissolves if the current is strong, and remains unattacked if the current is weak; but the amount of solution in all these cases is absolutely insignificant. Thus, with an iron wire of 8 square centimetres of surface, and with an intensity of current of 4 ampères, that is to say 50 ampères per square decimetre, the loss of weight after four hours was 0.018 grm., or about 1 m.grm. per ampère-hour.

If we make use of a diaphragm the attack on the metal is a little stronger; with 12 ampères per square decimetre, we found a loss of 5 m.grms. per ampère-hour, and 30 m.grms. with 30 ampères per square decimetre.

Thus it is well established that iron has only a negligible action on cyanide of potassium when used as an anode.

Electrolysis of Ferro- and Ferricyanides.—We know that the electrolysis of ferrocyanide of potassium with electrodes of platinum gives ferricyanide at the anode with a more or less considerable return; inversely, ferricyanide gives ferrocyanide at the cathode, with the formation of a blue deposit at the anode.

With electrodes of iron, this metal takes part in the reaction, and in both cases gives a variety of Prussian blue

at the anode, but only if we use a diaphragm; otherwise the alkali formed at the cathode decomposes this blue deposit, giving hydrate of iron.

Without a diaphragm we arrive at a state of variable equilibrium according to the conditions of the experiment. The same takes place with an alternating current, as we shall see later on, but in this case it is necessary to use an extremely high density of current.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 12.

HYDRONITRIC ACID AND THE INORGANIC TRINITRIDES.*

By I. M. DENNIS and A. W. BROWNE.

(Concluded from p. 313).

SUMMARY (continued).

C.—A Method for the Detection of Hydronitric Acid and the Inorganic Trinitrides.

In 1898 Curtius and Rissom (*Journ. Prakt. Chem.*, [2], lviii., 261) called attention to the deep red colouration produced either indirectly by shaking in air a solution of ferrous ammonium sulphate which had been treated with sodium trinitride, or directly by treating a ferric chloride solution with the same substance. From the red solution, boiling caused the precipitation of all of the iron as ferric hydroxide, and caused the red colour entirely to disappear. Even in the cold they found the colour faded gradually, and that a precipitate containing a basic ferric trinitride appeared. In a parenthetical clause they suggested that the production of this red colour was a "charakteristische Reaktion auf Stickstoffwasserstoff und auf Eisenoxydsalze."

In 1900 Curtius and Darapsky (*Journ. Prakt. Chem.*, [2], li., 408) again commented upon the blood-red colouration, produced this time by the action of sodium trinitride upon ferric ammonium sulphate in sufficiently strong solution. The coloured solution they again found to deposit a brown basic ferric trinitride, that appeared at once, if the solution was dilute, but only after some time if it was concentrated.

It has been found, on experimenting with the substances in this laboratory, that by observing the simple precaution of keeping the ferric compound in excess, the red colouration produced by the action of hydronitric acid or an inorganic trinitride will last indefinitely, even in very dilute solutions. If, for example, a ferric chloride solution of any desired strength is treated with hydronitric acid or the solution of a trinitride (also of any desired strength) up to the point only where the brown precipitate at first formed is re-dissolved when the solution is shaken up, then the colouration produced will last for weeks. The colour may vary, according to the strength of the solutions used, from a light reddish brown to a blood-red colour so deep that the solution, even in thin layers, appears almost black. In very concentrated solutions the odour of hydronitric acid may be perceived.

The action of an excess of the ferric salt in preventing the spontaneous precipitation of ferric hydroxide or a basic ferric trinitride from a solution of ferric trinitride is probably to be explained on the ground that the precipitation occurs as the result of hydrolysis, and that this is prevented by the addition of a salt with a common ion, which forces back the dissociation of the ferric trinitride.

This characteristic behaviour of a ferric salt toward the trinitrides has been of considerable use in this laboratory in testing residues and old solutions for hydronitric acid. It would also be of value in experimental work upon new methods of preparing the acid. In order to insure the perfect reliability of the test, a study has been made of some of the properties, physical and chemical, of the solution of ferric trinitride.

* From the *Journal of the American Chemical Society*, NXXI., No. 6.

The colour of the solution is remarkably similar to that of a solution of ferric sulphocyanate. When the colour intensity of the two is about the same, the eye, even with the aid of the spectroscope, can find no difference between them. The colour intensity of both solutions rapidly diminishes on dilution with water, that of the ferric sulphocyanate, however, fading more rapidly than the colour due to the ferric trinitride, as was ascertained by a series of careful experiments conducted with a Duboscq colorimeter. These facts may be readily explained on the assumption that the colour is in each case characteristic of the undissociated compound. Increasing the dilution would then not merely distribute the coloured bodies throughout a greater space, but would also, by increasing the dissociation, diminish their total number. Thus, diluting a given solution with its own volume of water would reduce the colour to less than one-half its former intensity. Moreover, since sulphocyanic acid is a much stronger acid than hydronitric, its salts will be dissociated to a greater extent for a given concentration (*Ann. Prakt. Chem.*, [2], 1885, xxxii., 300). Therefore dilution of a given solution of ferric sulphocyanate should cause a greater loss of colour than similar dilution of a solution of ferric trinitride of the same concentration.

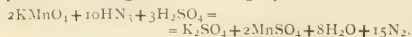
Concerning the sensitiveness of the ferric chloride test for trinitrides, it may be said that if one part by weight of N_3 be present in 100,000 parts of water, the addition of a little ferric chloride solution, insufficient in itself to produce any perceptible colouration, will, by the formation of ferric trinitride, produce a quite distinct colour, which may be clearly seen by looking down through the test-tube at a white background. Of course in dealing with such weak solutions it is necessary to take care not to mistake the colour of the ferric chloride solution itself for that of the trinitride. The danger may easily be avoided by adding the same amount of ferric chloride solution as that used in the test, to a volume of water equal to that of the solution to be tested.

With respect to the general applicability of the test it may be said that many representative inorganic trinitrides have been tested, including the potassium, sodium, barium, calcium, strontium, mercuric, cadmium, nickel, &c., as well as even the comparatively insoluble lead, silver, and mercurous compounds. In every case the characteristic red colouration has been quickly produced. Even in pyridine solution dry silver trinitride and ferric chloride act in the same way.

Dilute mineral acids (preferably hydrochloric acid), discharge the colour of ferric trinitride, but do not materially affect the colour of ferric sulphocyanate. On the other hand, mercuric chloride discharges the colour of ferric sulphocyanate more readily than it does that of ferric trinitride. By the aid of these reactions sulphocyanates and trinitrides may be identified even when both are present.

D.—The Reaction between Hydronitric Acid and Potassium Permanganate in the presence of Sulphuric Acid.

It seemed reasonable to suppose that hydronitric acid might be quantitatively determined by titration with potassium permanganate, and that the reaction would proceed according to the following equation:—



Preliminary experiments showed, however, that the amount of permanganate necessary for the oxidation of the hydronitric acid was considerably higher than that called for in the above equation, and the experiments described in this chapter were undertaken with a view to ascertaining the exact nature of the reaction.

The attempt was first made to determine the ratio between hydronitric acid and potassium permanganate in presence of sulphuric acid by ordinary methods of titration. An approximately tenth-normal solution of potassium permanganate was accordingly standardised with ammonium

ferrous sulphate. A dilute solution of hydronitric acid was standardised by precipitation of measured volumes with silver nitrate, evaporation of the washed precipitate with hydrochloric acid, and weighing as silver chloride.

Titrations were made by the following methods. (In each case sulphuric acid was added in sufficient quantity to keep the solution quite strongly acid throughout the experiment). 1. By adding a measured amount of hydronitric acid to a measured excess of potassium permanganate, (a) at room temperature (20°), and (b) at a temperature of 45°. The excess of permanganate was subsequently determined by back titration with standard ammonium ferrous sulphate solution. 2. By gradually adding hydronitric acid to a measured amount of permanganate until the colour was just destroyed. 3. By adding hydronitric acid in slight excess to a measured amount of permanganate and then adding more permanganate, drop by drop, until the faintest discernible permanent colouration was produced. In each case the reaction took place only after the lapse of several minutes. Raising the temperature hastened the reaction to some extent, and apparently had no other effect. At temperatures much above that of the room it was considered advisable to keep the reacting substances in a stoppered flask provided with a U-tube containing silver nitrate solution, in order to detect any loss of hydronitric acid during the titration. No loss was found to have occurred in any of the experiments. The results of the titrations are given in Table V.

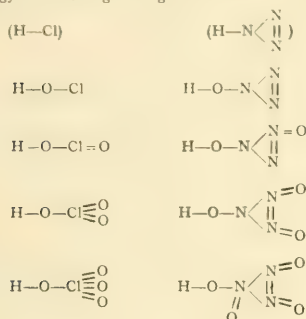
TABLE V.

Number of experiment.	Number of different titrations made.	Ratio of molecules of HN_3 to one molecule of $KMnO_4$.	
		Extremes.	Average.
1a	5	2'12—2'22	2'18
1b	6	2'10—2'29	2'21
2	10	2'11—2'39	2'25
3	5	2'40—2'60	2'47
Average from the twenty-six titrations, 2'27			

From the foregoing results it will be seen that this method of ascertaining the ratio between the two reacting substances is rather unsatisfactory. Both the variations within a given series of titrations, and the variations of the averages of different series, seem to be outside the limits of experimental error. The difficulty is no doubt due to the impossibility of securing a definite end-point, owing to the extreme slowness of the reaction toward the end of the titration. It is probably also due, in some degree, to a tendency on the part of the reacting substances to unite in different proportions under different conditions, as when, for example, one or the other may temporarily or locally be in excess during the titration. Further reason for this view will be seen later. The method employed in the first experiment was found to be doubly unreliable because of the fact that when hydronitric acid is added to potassium permanganate in excess, there are thrown down oxides of manganese of varying composition which are insoluble alike in sulphuric and hydronitric acids. (This is true even when there is a considerable excess of sulphuric acid present in the solution during the titration).

The titration experiments were now discontinued, and a qualitative study made of the reaction products formed. The solution, obtained by allowing a slight excess of hydronitric acid to act upon a quantity of potassium permanganate solution in the presence of sulphuric acid, and then destroying the excess of hydronitric acid by adding permanganate drop by drop until the characteristic colour was just discernible, was examined as follows. It was not considered necessary to look for free N_3 among the reaction products, for it does not seem reasonable to suppose, with Dennstedt and Göhlich (*Chem. Zeitung*, xli., 876), that the monovalent nitrene group, similar in so many respects to the chlorine atom, could exist alone, even if the hydrogen atom could be removed from hydronitric acid without breaking it up. There would probably

be immediate union of two such groups, as suggested by other investigators (Curtius, Hantzsch, and others), to form a compound, $(N_3)_2$, which we have called nitrine, analogous to the chlorine molecule. It was, however, theoretically possible that, during the oxidation of the hydronitric acid, certain oxyacids might have been formed, analogous to the oxyacids of chlorine. To show the analogy the following list is given:—



In these compounds the nitrine group would show, according as none, one, two, or three of its nitrogen atoms became pentavalent, a monovalent, trivalent, pentavalent, or heptavalent character, just as the chlorine atom is supposed to do.

To ascertain whether any such nitrogen acids were formed by the action of permanganate upon hydronitric acid, portions of the solution whose preparation was described in the first lines of the preceding paragraph were carefully distilled (a) at temperatures of 70° and 100°, respectively, at ordinary atmospheric pressure, and (b) at temperatures of 50° and 80°, respectively, at a pressure corresponding to 10 c.m. of mercury. The vapours were in each case led into water containing a little phenolphthalein with just barely enough sodium hydroxide to render it. In no case was the red colour destroyed. The absence of nitric acid was still further established by the fact that the test with ferrous sulphate solution and concentrated sulphuric acid repeatedly gave negative results.

To show that none of the nitrogen had been changed to ammonia, or to some other nitrogen base, with consequent formation of ammonium sulphate or a sulphate of the base, a part of the solution was distilled with calcium hydroxide. The distillate gave no alkaline reaction.

From the foregoing experiments it was a legitimate inference that the hydrogen of the hydronitric acid had gone to form water, and that the nitrogen had been given off as gas, either as free nitrogen, or one of its non-acid-forming oxides.

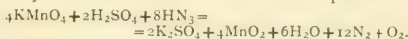
During the titration experiments, described above, it had been observed that minute bubbles of the gas were slowly evolved as the decolorisation took place. These were at first thought to be bubbles of hydronitric acid escaping from the solution as the result of the action of the sulphuric acid, until the use of stoppered flasks with U-tubes, containing silver nitrate solution, proved the contrary. Shaking the flask during the progress of the reaction, even after decolorisation was complete, caused a comparatively brisk evolution of gas to take place.

The composition of the gas was determined qualitatively by collecting a quantity in a Hempel pipette, and treating it successively with the following series of reagents: Alcohol, water, caustic potash, alkaline pyrogallol, fuming sulphuric acid, and cuprous chloride. Contraction took place only after passing it through the alkaline pyrogallol. This indicated the presence of oxygen. The residues

obtained by treating in this way gases evolved from reacting mixtures (of HN_3 , $KMnO_4$, H_2SO_4) in which either the hydronitric acid or the potassium permanganate, respectively, was present in excess, showed no change in volume when mixed with either equal or double volumes of hydrogen, and subjected to the action of the electric spark in a Hempel explosion pipette. This showed quite conclusively that no oxides of nitrogen were present, a fact that already had seemed probable from the circumstance that no contraction had occurred in any case when the gas had been passed through alcohol or water. The residue, then, consisted of nitrogen.

To ascertain the quantitative composition of the gas under different conditions (*i.e.*, according as one or the other of the reacting substances was present in excess in the mixture from which the gas was evolved), portions were simply shaken with alkaline pyrogallol, and the volume measured before and after the operation.

It was found, in general, that when the permanganate was present in excess the percentage of oxygen in the gas mixtures evolved was not very constant. The insoluble higher oxide of manganese that appears under these conditions is, therefore, in all probability, of variable composition. While the results of a series of four experiments in which the permanganate was taken in excess, vary in a way that seems to indicate that the ratio between the amounts of hydronitric acid and potassium permanganate entering into the reaction in different cases is not a constant one under these conditions, still the data accord fairly well with the amounts indicated in the equation—



This equation is not far from agreement with the results of titration given in Table V. under the heads 1a and 1b. These results were also obtained with permanganate in excess.

When hydronitric acid was taken in excess, the results were more satisfactory. A series of experiments were made to determine the ratio of nitrogen evolved to permanganate reduced, when hydronitric acid was in excess. The composition of the gas evolved was found to be 92 per cent nitrogen (by volume) and 8 per cent oxygen. Knorre and Arndt (*Ber.*, 1900, xxxiii., 30), in somewhat similar work on the oxidation of hydroxylamine by various agents, devised a special form of apparatus to serve the double purpose of measuring the gas evolved and preserving it free from air or other gases for subsequent analysis. In our work, however, this was not necessary, as the gas mixture, evolved under certain conditions in a Hempel pipette, was analysed separately, without making any effort to measure the total volume. The total volume of gas evolved from a measured amount of the same reacting mixture, under similar conditions, was then measured in an ordinary Lunge nitrometer. To ascertain the amount of nitrogen evolved, the volume of oxygen, calculated from the results of analysis, was subtracted from the total volume. In using the nitrometer care was taken to immerse the evolution bottle in a constant temperature bath before each reading. During the reaction the bottle was frequently shaken to facilitate evolution of the gas. To test whether any appreciable quantity of the gases remained in solution, additional experiments were performed, in which a small Erlenmeyer flask was substituted for the evolution bottle. One of the reacting substances was placed in the flask, and the other in a small test-tube standing upright within the flask. By inclining the flask, the two solutions were mixed. After the reaction was complete, the solution was heated nearly to boiling, and then permitted to cool down to the initial temperature. The volume of gas evolved was not appreciably greater than when the evolution bottle was used and the solution not boiled. Therefore no appreciable amount of gas had remained in solution.

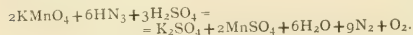
In Table VI. are given the results of a series of experiments showing the ratio, as obtained above, between

nitrogen evolved and permanganate reduced when hydronitric acid is in excess.

TABLE VI.

Number of experiment.	Cubic centimetres KMnO_4 taken.	Cubic centimetres gas evolved.	Cubic centimetres nitrogen evolved.	Molecules N_2 per molecule KMnO_4 .
1	24.6	24.7	22.7	4.54
2	25.0	25.1	23.1	4.56
3	24.5	24.7	22.7	4.56
4	24.7	24.1	22.2	4.44
5	22.4	22.2	20.4	4.49
6	20.2	20.1	18.5	4.51
Average.				4.52

From these results it will be seen that when hydronitric acid is in excess the ratio potassium permanganate to hydronitric acid is smaller than when the permanganate is in excess; that is, in the former case a given amount of permanganate will act upon more hydronitric acid than in the latter case. This conclusion is also indicated in a rough way by the results given in Table V., where we find the ratio to have smaller values when potassium permanganate is in excess than when equivalent amounts are taken, or when hydronitric acid is virtually in excess. The following equation best represents the results given in Table VI. :—



To obtain a further check upon this equation the ratio between potassium permanganate and hydronitric acid (the latter in excess) was determined by adding a measured amount of a standardised solution of the former to a measured excess of the latter, and determining the excess of hydronitric acid by precipitation with silver nitrate in the usual way, after the reaction had taken place. The results of the two experiments performed are given in Table VII.

TABLE VII.

Number of experiment.	Cubic centimetres KMnO_4 taken.	Cubic centimetres HN_3 taken.	Cubic centimetres HN_3 oxidised.	Molecules HN_3 per molecule KMnO_4 .
1	24.6	49.0	17.2	3.08
2	25.0	48.8	16.7	2.94
Average.				3.01

These results show close agreement with those given in Table VI., and point toward the same equation. Moreover, by combining the results of Table VI. and VII. it may be proved that under the conditions of the experiments no polymeric nitrogen is evolved, for if 1 molecule of permanganate oxidises 3 molecules of hydronitric acid, as indicated by Table VII., causing the evolution of 4.5 molecules of nitrogen gas, as indicated in Table VI., then for each molecule of hydronitric acid oxidised there are produced 1.5 molecules of nitrogen. Hence all the nitrogen of the acid appears as diatomic nitrogen. A density determination made according to the method of Dumas confirmed this conclusion.

Only one experimental fact is not in close accord with the above equation. Upon inspection of the equation it will be seen that in the mixture of gases evolved during the progress of the reaction there should be 10 per cent (by volume) of oxygen and 90 per cent of nitrogen. Experimentally, however, the mixture was found to contain about 8 per cent of oxygen and 92 of nitrogen. No explanation of the error has been found, but it is not to be considered as sufficiently serious to cast doubt upon the validity of the equation as given above.

It is apparent from the results of these experiments upon the reaction between hydronitric acid and potassium permanganate that the latter agent can not be used for the accurate quantitative determination of the acid. The results are of theoretical interest, however, because of the light that they appear to throw upon the structure of potassium permanganate, a subject that will be discussed by the authors in a later paper.

ELECTROLYTIC PREPARATION OF TIN PASTE.*

By F. GELSHARP.

TIN paste is used for the production of metallic or silvered paper, having the appearance of tin or lead foil, and it is also used for ornamental purposes.

As I believe members are interested in any process in which electro-chemistry advantageously takes the place of the older chemical methods, I beg to bring before the Faraday Society the following description of a process for manufacturing tin paste which was specially designed for a firm of paper makers.

The oldest method of making tin paste was that carried out by the natives of India. They melted block tin at a high temperature, and poured it into a wooden box, which was then shaken vigorously; the tin was thus converted into very fine shot and dust. The finer particles which they used for the paste were separated from the coarser granules by gravitation by means of water. It was afterwards dried and mixed with a weak solution of glue, and in this state it was ready for use. This they used as a paint, the article to be ornamented was coated with it, and after being dried it was burnished.

The chemical process for making tin paste as generally carried out in this country is as follows :—The commercial ingot is reduced to what is known as feather tin by melting it and then allowing it to fall some distance. The tin in this form is dissolved in strong hydrochloric acid, with the aid of heat, in copper vessels, and a concentrated solution of stannous chloride thus obtained. The liquid is diluted and the tin precipitated in the form of paste by introducing metallic zinc. The process is troublesome on account of fumes, and, moreover, does not give the whole of the precipitated tin in the form of paste, but partly as bright metallic feathers and crystals, which have to be worked over again; whereas in working the electrolytic process about to be described there are no fumes, and the paste is perfect in every respect. Further, the process is not so costly, and can be worked continuously, the deposited paste being removed at intervals without stopping the current.

The electrolytic process is similar to the electro-refining of metals. Anodes of tin are dissolved in an electrolyte of dilute hydrochloric acid, and the tin is deposited in the form of a sponge or paste on cathodes of the same metal. The spongy deposit is lighter than the electrolyte on account of the hydrogen it contains, and consequently floats on the surface of the solution after being detached from the face of the cathodes, so that it can be conveniently removed without breaking the current.

An apparatus capable of producing 20 cwt. of tin paste per week consists of a generating plant giving 1500 amperes at 8 to 10 volts. There are five vats, which are worked in series, and are made of slate or pitch-pine wood 106 × 106 × 91.5 c.m. deep (3 ft. 6 in. × 3 ft. 6 in. × 3 ft. deep), each containing four anodes and five cathodes coupled in parallel.

The anode plates are about 2.5 c.m. (one inch) thick, roughly cast from commercial ingots of tin; the surface exposed to the electrolyte being 91.5 × 76 c.m. (3 ft. × 2 ft. 6 in.).

The cathode plates are of block tin or tinned iron, the active surface being 91.5 × 76 c.m. (3 ft. × 2 ft. 6 in.).

The anodes are supported at the two top corners, and in each vat are all connected to one conductor.

The cathodes are supported by and soldered to copper conductors, which are all connected to a main conductor. These main conductors are of circular copper bars 3.2 c.m. (1.4 in.) in diameter.

The electrolyte is a dilute solution of hydrochloric acid in 5° Tw., which must be free from arsenic.

The current density is 270 amperes per square metre, or 25 amperes per square foot of cathode surface.

As the anodes are dissolved away they are removed before they crumble and fall to pieces, and what remains

* A Paper read before the Faraday Society, December 19, 1904.

of them is melted up with fresh ingots and cast, to form new anodes.

The electrolyte is kept in circulation by means of a small turbine or plunger pump of lead or block tin driven by a small motor; the liquid is drawn from the bottom of the vats, and discharged into the top; this is found necessary, as otherwise the electrolyte at the bottom of the vats would soon become very rich in tin, and instead of tin paste at the lower parts of the cathodes there would be crystal or leaf tin deposited.

When the deposited tin sponge has grown to about an inch in thickness it is detached from the cathodes by means of a T-shaped scraper, which is pushed down the face of the cathode plates; the floating spongy tin is removed from the surface of the vat by means of a perforated scoop to prevent short-circuiting of the current through the floating tin; the cathode plates are varnished or painted with a non-conducting material from 5 to 7.5 c.m. (2 or 3 inches) below the surface line. The tin paste is allowed to drain, and is then thoroughly washed with water, and dried to make it ready for use.

This may not seem to be an efficient way of utilising the electric current, because the current-efficiency is only about 50 per cent; but any attempt that I have made to produce tin in the form of paste or sponge at a higher efficiency has been futile; it appears to be necessary to have hydrogen deposited along with the tin, for when no hydrogen is deposited the tin comes down in a crystalline or bright leaf-like form.

A METHOD FOR THE DETERMINATION OF CHLORIC ACID.

By W. S. HENDRIXSON.

In the methods for the determination of chloric acid by reduction, metallic zinc, in some form, and ferrous sulphate have been the reducing agents most used, though several others, including sulphur dioxide and formic aldehyde, have been employed. The conditions under which zinc and ferrous sulphate have been used have been much varied. Thorpe (*Journ. Chem. Soc.*, xi., 541) and Thorpe and Eccles (*Journ. Chem. Soc.*, xiv., 856) used the zinc-copper couple to reduce chlorates, and determined the chloride, resulting from the chlorate, with a solution of silver. Bothamley and Thompson showed that the results by this method were too low unless sulphuric acid was added near the end of the reduction to dissolve any basic salts of zinc (*Journ. Chem. Soc.*, liii., 164). By the same method, Becker also found the results too low, and preferred to use zinc dust and a little copper sulphate (*Repert. Anal. Chem.*, i., 377). Fleissner used zinc dust and boiled the solution one hour (*Zeit. Anal. Chem.*, xx., 115), but Becker attained complete reduction only by using a large excess of zinc dust with sufficient sulphuric acid to dissolve it completely without the aid of heat.

Stelling reduced chlorates by long boiling with ferrous sulphate, in alkaline solution, and determined the resulting chloride (*Zeit. Anal. Chem.*, vi., 32). Becker found that the reaction was very slow and incomplete, and recommended a neutral solution of ferrous sulphate. Carno reduced the chlorates in bleaching powder by heating at 100° with a large excess of ammonium ferrous sulphate and an excess of sulphuric acid (*Comptes Rendus*, cxxiii., 449). The amount of chlorate was found either by titrating the resulting chloride by the method of Volhard, or by determining the excess of ferrous sulphate with permanganate. Rosenbaum states that chlorine will be lost in this method of reduction if the acid and the ferrous sulphate are added to a hot solution of the chlorate (*Zeit. Angew. Chem.*, 1893, 80).

In the course of my work on the action of chloric acid on metals, it was observed that metallic iron very readily reduces free chloric acid even in very dilute solutions

(*Journ. Am. Chem. Soc.*, xxvi., 747). At ordinary room temperature the solution of the metal is very rapid in moderately concentrated solutions of the acid, and the iron goes at once into the ferric condition, as was proved by many tests while solution was going on. No gas is evolved, but the iron simply disappears, and there results the yellowish-brown solution of ferric salt, and the solution remains clear if the acid is in considerable excess. Whether iron alone thus reduces chloric acid completely could not be determined with accuracy, owing to the fact that toward the end of the reaction large amounts of oxide and possibly basic salt are necessarily formed, and these make it impracticable to obtain a solution suitable for titration with silver without the use of agents which would also decompose chloric acid. An approximation, however, showed that at least 95 per cent of the chloric acid was reduced. These facts suggested that the determination of chloric acid might be brought to a very simple form by using metallic iron as the chief reducing agent in the presence of an excess of sulphuric acid, which would prevent the formation of insoluble compounds, make the method applicable to chlorates by setting free the chloric acid, and form ferrous sulphate, which is itself a reducing agent for chloric acid, and which would already be present to serve, when oxidised, as the indicator in the titration of the chloride formed, by the method of Volhard. It is evident, therefore, that such a method would be a very simple combination of the two general methods already mentioned, the reduction of chloric acid by a metal, and probably a more efficient one than zinc, and the reduction by ferrous sulphate.

To carry out the method a weighed amount of pure potassium chlorate or a measured volume of chloric acid of known strength was placed in a small flask with about 50 c.c. of pure sulphuric acid having a concentration of about 10 per cent, and an excess of "card-teeth" used in most laboratories as a convenient form of iron. In some of the experiments recorded below, the flask was fitted with a delivery-tube which dipped into water, the purpose being to prevent the possible loss of hydrochloric acid, a precaution which at room temperature was proved to be wholly unnecessary. At first ferric salt is formed, and gives the solution the characteristic colour due to ferric salts, but the salt is soon reduced and the solution becomes colourless or slightly green. If all the chlorate is dissolved at the beginning of the experiment, the disappearance of the yellow colour may be taken to mark the end of the reduction, which requires, at room temperature, about one hour. No doubt the reduction could be hastened by heating, if precaution were taken to prevent the loss of hydrochloric acid by volatilisation. As might naturally be expected, the method serves quite as well for bromic acid and bromates as for chloric acid and chlorates, and two determinations of the bromic acid in potassium bromate are given below.

After the reduction was completed the solution was made up to a definite volume, and portions of it were titrated with N/20 silver nitrate by Volhard's method. Usually an excess of silver was added before the iron was oxidised with an excess of nitric acid to the ferric condition to serve as the indicator. There seems, however, to be little danger of the loss of chlorine if the nitric acid is added before the silver.

The following are results obtained by the method described, the amounts of silver required in the titrations being calculated to chloric acid or bromic acid:—

1. 5 c.c. of a solution of chloric acid gave 1.0639 grms. HClO_3 .
2. 5 c.c. of the same solution gave 1.0619 grms. HClO_3 . The same solution, titrated with standard barium hydroxide, gave, in 5 c.c., 1.0665 grms. HClO_3 .
3. 0.4595 grm. KClO_3 gave 0.3158 grm. HClO_3 ; calculated, 0.3165 grm.
4. 0.6709 grm. KClO_3 gave 0.4628 grm. HClO_3 ; calculated, 0.4622 grm.
5. 0.8300 grm. KClO_3 gave 0.5731 grm. HClO_3 ; calculated, 0.5718 grm.

6. 1.2744 grms. KClO_3 gave 0.8778 grm. HClO_3 ; calculated, 0.8778 grm.
 7. 0.3350 grm. KBrO_3 gave 0.2605 grm. HBrO_3 ; calculated, 0.2585 grm.
 8. 1.0983 grms. KBrO_3 gave 0.8460 grm. HBrO_3 ; calculated, 0.8478 grm.

The method above described seems to have some advantages. It is extremely simple. It can be carried out at room temperature, avoiding any danger of the loss of hydrochloric acid by heating. In the reduction and the preparation of the solution for titration are necessary only iron and pure sulphuric and nitric acids, which are always at hand in every laboratory, and no filtering or other operations likely to occasion loss of chlorine or loss of time are required.

Perchloric acid shows the same indifference toward metallic iron as toward most other reducing agents, and does not therefore interfere in the determination of chloric acid by this method.—*American Chemical Journal*, xxxii., No. 3.

A RAPID METHOD FOR THE DETERMINATION OF TOTAL SULPHUR IN IRON BY EVOLUTION.

By S. S. KNIGHT.

THE recent modification of the method for determining sulphur in iron, presented by Walters and Miller, of Pittsburgh, Pennsylvania, had as its principal disadvantages the extraordinarily long time, which they claim would be at least an hour, under the most favourable circumstances, to complete a sulphur determination, and also the expensive and unusual apparatus for roasting samples in a current of reducing gases.

In commercial laboratories which are not equipped with this apparatus, the recent modification of this roasting process has consisted in roasting the weighed sample for a period of one hour at a slowly increasing temperature. The culmination of this annealing process was the highest heat obtainable before a blast-lamp, which was continued for at least fifteen minutes. The sample thus roasted was treated as heretofore by the evolution process.

In the laboratory of the Birmingham Pipe and Casting Company, the writer has been able to get results which check very closely with those obtained by the above-described method, and also with those obtained by the barium chloride gravimetric method, by the following process:—

The weighed sample, which in our case consisted of 2 grms., was mixed with 1 grm. of the purest obtainable iron dust by hydrogen, and in which the sulphur content had been previously determined. This mixed sample is then placed in a small porcelain crucible and 1 grm. more of the iron by hydrogen is sprinkled over the top so as to form a continuous covering. On top of this is placed a small disc of quantitative filter-paper, the lid is then placed on the crucible, and this is placed on the triangle over the blast-lamp. For ten minutes the highest heat obtainable with the blast-lamp is used in roasting this mixture, at the expiration of which time it is allowed to partially cool, and the contents of the crucible are then placed in the ordinary evolution-flask and treated with hydrochloric acid, while the evolved gases are washed in any of the common forms of absorption bulbs. The absorbent liquid in our case has been an ammoniacal solution of cadmium chloride, which was afterwards titrated with the iodine solution of known strength. The results obtained by this method are exactly those given by standard gravimetric methods and also the same as those obtained by Walters and Miller's method, while the time consumed is something less than one-half hour from the time the sample arrives in the laboratory.

It is believed by the writer that the advantage of this

modification will be readily appreciated by chemists in charge of commercial laboratories.—*American Chemical Journal*, xxxii., No. 1.

NOTICES OF BOOKS

A Chemical Conception of the Ether. By Professor D. MENDELEEF. London: Longmans, Green, and Co. Pp. 51.

As is well known, Prof. Mendeleef has classified the known elements into groups and series in accordance with their atomic weight and chemical properties. Following out this classification he endeavours to show that two of the places in his "zero" group may be assigned to coronium and ether, both of which would have atomic weights much less than hydrogen, and, in consequence of their great molecular velocity, could not exist on the earth, though they might on the sun and the more massive stars, or even, in the case of ether, be too volatile to be retained by any known star. Be it noted that this is merely a speculation, and we have deliberately used the permissive phrase "may be," as we do not gather that the author would "father" any more definite expression. We see no reason why there should not be many elements in series "o" and possibly "o o" of less atomic weight than hydrogen—elements which could not exist in a free state on the earth, and possibly coronium does represent one or more of those elements; but as regards ether, our speculation has led us in a different direction; we consider ultimate matter to consist of at least two—possibly more—infinately rigid, absolutely elastic substances of different masses; of these ether is the least massive, and is not subject to gravity, being itself the cause of gravity; that is to say, gravity is the resultant of its blows on the more massive substance or substances; whilst ponderable matter consists of the more massive substance or substances. Here we are more in accord with Lord Kelvin than the author, for the latter considers all matter to be subject to gravity, whereas the former does not, though we should not care to claim any close approximation in the details of our respective conceptions of the ultimate constitution of matter.

At present all such speculations are speculations pure and simple, nor do we see any likelihood of subjecting any of them to physical tests.

What is the essential condition that an atom "A" will combine with an atom "B" when "C" is absent, whereas the addition of "C" will separate "A" from "B" and form a combination of "A" and "C"—all these retaining their individuality throughout? We do not know; and until we do know, we cannot say whether a purely kinematical conception of matter is satisfactory.

Food Inspection and Analysis. By ALBERT E. LEACH, S.B. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

THE student of dietetics, as well as the public analyst, will have much reason to be grateful to the author of this work for the admirable treatise he has produced. Besides containing the details of the most satisfactory methods of determining the constituents of almost every variety of food material and detecting common adulterations, it includes much information concerning the values of different kinds of foods which is not as a rule to be found in text-books of food analysis, and which will be no doubt specially appreciated by the food economist. Thus the composition of flesh foods and eggs are fully discussed, numerous tables being given to show the proportions of the constituents of various kinds of meats and meat preparations; directions are given for the detection of horse flesh when mixed with other meats, and also hints for discriminating between frozen and fresh meat. The

work compares most favourably both in choice of material and in treatment with other similar text-books, and it possesses the great attraction of presenting its information in a very concise form, unnecessary matter, such as the discussion of superseded methods, or of modifications of existing methods, which have not yet been thoroughly tested, being rigidly excluded. At the same time the short descriptions of manufacturing processes for the preparation of various food materials are well worth the space allotted to them, as being likely to indicate probable and possible impurities. A chapter is devoted to colouring matters in general, and another to preservatives, and it is suggested that in all cases in which adulterations are found the analyst should determine—at any rate, approximately—the amount present, so that determination as well as detection methods are always included. The photomicrographs form a very characteristic feature of the book. They include, firstly, illustrations of powdered food and food products, and also powdered adulterants; secondly, typical adulterated foods, which will be found most useful; and thirdly, sections of foods and adulterants. By careful study of these plates and the preparation of similar slides, the student should be able to make himself familiar with the appearance of the more common substances under the microscope, the use of which in food analysis is rightly strongly advocated. The author having had experience in one of the best food laboratories existing, has undoubtedly had unique opportunities of estimating the various advantages offered by one method over another, and has evidently thoroughly tested the various methods in use, so that when he shows a decided preference for any modification—as, for example, in the determination of the total solids in milk—it may be confidently assumed that there is a good deal to be said for his view.

A Select Bibliography of Chemistry, 1492—1902. Second Supplement. By HENRY CARRINGTON BOLLON. City of Washington: Smithsonian Institution. 1904.

THIS supplement includes the years 1898 to the end of 1902, and preserves the same sub-divisions as were adopted in the main work. It thus contains the titles of new chemical books and academic dissertations, and also new editions published in the above years, arranged in separate classes according to the special nature of their contents, the majority of the works being either in the English, French, German, or Italian languages. Since the death of the author in 1903, while the book was in press, Mr. Axel Moth, of the New York Public Library, has prepared an alphabetical subject index for the supplement, which affords a means of readily ascertaining the titles of recent publications dealing with practically any subject of interest to chemists.

Traité Élémentaire de Physico-Chimie. ("An Elementary Treatise on Physical Chemistry.") By EMM. POZZI-ESCOFF. Paris: Ch. Béranger. 1905.

IT must be seldom indeed that a book issues from the press disfigured as this is by so many misprints. The cases of incorrectly spelt names reach an almost incredible number. Thus we find such specimens as "Latmier-Clarck," "Arenius," "Debieune," "Baknis Roosevelt," "Kohlrauch," "Kelvin," "Van der Waal," "Stass," and though these names are so well known to chemists that the errors are not perhaps of much real consequence, the matter assumes a somewhat different aspect when we find Proust's hypothesis ascribed to Proust, who, moreover, is described as an English chemist, whereas the real Proust was a native of Angers. The same extraordinary carelessness extends to many of the chemical equations; taking, as an example, those on page 47, where the principle of the construction of an equation is illustrated by the action of potassium bichromate on ferrous chloride; in the equation and the few lines of explanation following it there are no fewer than ten separate errors, the result

being that a beginner would probably be hopelessly puzzled. In the text there is to be found no compensating lucidity or novelty of the treatment of the recent wonderful developments of physical chemistry, unnecessary attention being paid to the exposition of exploded theories. Moreover, quite apart from printer's mistakes, there are many examples of actually incorrect statements, some of them of a serious nature; for instance, in the discussion of the constants of dissociation, no definition or explanation whatever is given of the meaning of K when this symbol is first introduced, though some hundred pages later, separated by totally irrelevant matter, we find a short definition of it as an ionisation constant. There being no alphabetical index to refer to, on a first reading the reader could only regard the values as so many numbers; nor are they even the correct numbers, for though given as K they are really the values of $K \times 10^3$; also, in the case of maleic and fumaric acids the constants relate to different dilutions and are thus totally misleading. These and other equally glaring mistakes show how very much revision is necessary before the book can fulfil its purpose of raising the intellectual level of the masses of French chemists, which the author states in the preface was the special aim he kept before him.

The Chemistry of Gas Manufacture. A Practical Handbook on the Production, Purification, and Testing of Illuminating and Fuel Gas, and on the By-products of Gas Manufacture. By W. J. ATKINSON BUTTERFIELD, M.A., F.I.C. Third Edition, with Illustrations. Volume I. *Materials and Processes.* London: Charles Griffin and Company, Ltd. 1904. Pp. 257.

THIS handbook has been revised and enlarged to such an extent that it can no longer be published conveniently as a single volume; therefore it was decided to publish the portion treating of the materials and processes of gas manufacture at once, to be followed by a second volume on "The Testing and Use of Gas."

The volume now before us, Part I., is divided into seven chapters. The first chapter deals with the raw materials of gas manufacture, the chief of which is, of course, coal; though cellulose, wood, peat, &c., also claim a certain amount of attention. Chapters II. and III. are devoted wholly to coal-gas, and all the various artifices and appliances used in its manufacture and purification.

Chapter IV. is on carburetted water gas and its method of manufacture; in this connection we must express our surprise that the important and well known "Mond" process is not given; in fact the only reference we have been able to find to it is on p. 125, where mention is made of the amount of ammonia obtained from the Mond gas producers.

Chapter V. is on oil-gas, and here we have several processes described, such as those of Pintsch, Pope, Keith, Tatham, and others.

Enriching by light oils is the subject of Chapter VI., while in Chapter VII. we find the final details of the manufacture and sundry schemes for making and enriching gas.

The book will no doubt be useful to those engaged in gas making, as it is clearly written and well arranged. There is a table of contents, and an index of thirteen pages.

Analysis of Foods, and the Detection of Adulteration. ("Analyse des Matières Alimentaires et Recherche de Leurs Falsifications.") By CH. GIRARD, with the collaboration of MM. Sangle-Ferrière, de Brévaux, Truchon, V. Genin, Pons, de Raczkowski, Leys, Froidevaux, Cuniasse, and Lefaye. Second Edition, considerably enlarged. Paris: Vve. Ch. Dunod. 1904. Pp. 871.

THE success achieved by the first edition of this work has encouraged the author to bring out a much larger second edition; the new volume contains nearly 200 pages more than the old one. All the original articles have been supplemented and brought up to date, and the very latest

apparatus and methods for food analysis are fully described. New articles have been added on the analysis of water, milk, jam, &c. Without going through the whole list, we may point out that this volume deals with the examination of all kinds of foods and drinks; wine, beer, cider; bread, butter, cheese; pastry, coffee, cocoa, sugars, spices, colours, and soldering materials, &c.

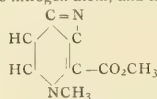
Independently of the chemical analysis proper, there is a section on bacteriology, while the bibliographical portion is well conceived and arranged. Altogether we have a work of considerable importance and of undoubted value to those engaged in food analysis.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

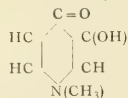
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 21, November 21, 1904.

Constitution of Ricinine.—L. Maquenne and L. Philippe.—In a former paper the authors described the formation of what they believed to be a methyloxypyridone from ricinine. They find that this substance is a very feeble base, but its bromo- and nitro-derivatives are distinctly acid in character. Phosphorus pentachloride converts it into a dichloropyridine, $C_5H_3Cl_2N$. The formation of this compound shows that methyloxypyridone has lost a methyl group during chlorination, and therefore the latter must have been attached to the nitrogen atom and not to the carbon of the chain. This dichloropyridine can be reduced to pyridine by means of hydriodic acid and red phosphorus. The authors conclude that methyloxypyridone is a derivative of a hypopyridine in which a methyl group is attached to the nitrogen atom, and therefore that—



is the structural formula of ricinine, and—



of methyloxypyridone.

Chemical Composition of Radio-active Gaseous Mixtures arising from Hot Springs.—Ch. Moureu.—Analyses of several of these mixtures are given. They all contain helium, as would be expected from recent researches upon the production of helium by spontaneous change of the radium emanation. The author proposes later to estimate the helium in these mixtures at different stages of the decay of the radio-activity.

Influence of the Nature of the Anode upon the Electrolytic Oxidation of Potassium Ferrocyanide.—André Brochet and Joseph Petit.—When potassium ferrocyanide is electrolysed, potassium ferricyanide, oxygen, and hydroferrocyanic acid appear at the positive pole. If the anode is a metal which can be attacked by the anion $[\text{Fe}(\text{CN})_6]^{4-}$, the corresponding ferrocyanide is produced, the quantity of potassium ferricyanide simultaneously formed varying with the metal used. Results of experiments, using various metals as anode, are given, and the metals classified according to their behaviour towards the ion $[\text{Fe}(\text{CN})_6]^{4-}$.

Complexity of Dissolved Sulphates.—Albert Colson.—A solution was prepared containing 0.75 molecule of

CuSO_4 in two litres of water; the lowering of the freezing-point was found to be 0.70° . The copper was then precipitated by an exact amount of H_2S , and the lowering of the freezing-point of the sulphuric acid solution was determined. It was found to be 1.51° , i.e., twice that of the copper sulphate solution. Since by analysis 1 atom of copper corresponds to 1 molecule of sulphuric acid, the formula of the dissolved metallic salt must be $(\text{CuSO}_4)_2$. Similar results were obtained with other metallic sulphates.

The Influence of certain Substances in Promoting or Retarding the Production of Rust.—L. Lindet.—Some metals, such as copper, when placed with iron in aerated water, promote the formation of rust; others—such as lead, zinc, and principally arsenic—retard its formation. The author finds that these effects are really due to the solution of traces of the hydroxide of the metal in the water. He discusses the formation of rust in tin-plated or galvanised iron vessels containing impure alcohol.

Action of Iodine and Yellow Oxide of Mercury upon Acids of the Ethylene Series.—J. Bougault.—This reagent does not affect acids of this series having the general formulæ $\text{R}-\text{CH}-\text{CH}-\text{COOH}$ or $\text{R}-\text{C}(\text{CH}_2)-\text{COOH}$. Acids with a β -ethylene linking yield iodo-lactones of the general type $\text{R}-\text{CH}-\text{CHI}-\text{CH}_2-\text{CO}$

The formation of these lactones gives a rigorous and easy method of separating the β -acids from the $\alpha\beta$ -acids which are often mixed with them. The β -acids can be re-generated from the lactones by means of zinc and acetic acid.

Action of Hydrobromic and Hydrochloric Acids upon Triacetin.—R. de la Acena.—The preparation and properties of several new halogen compounds of triacetin are described.

Action of Pyridine and Quinoline Bases upon Bromo-succinic and Dibromo-succinic Ethers.—Louis Dubreuil.—The three bases studied—pyridine, quinoline, and quinaldine—act in the same way upon these ethers, i.e., they remove the hydrobromic acid, and cause the formation of non-saturated ethers. At the same time quinoline and quinaldine are transformed into basic hydrobromides, similar to the basic hydrochloride of aniline recently described by Selivanof.

Theory of Dyes.—Jules Schmidlen.—According to this theory, the molecule of a true dye contains an endothermic group with double aliphatic carbon linkings (a chromophore) which is the cause of the colour, and also a very exothermic group (an auxochrome), the presence of which renders the endothermic group stable.

Action of Reduced Nickel upon Aromatic Ketones.
A New Synthesis of Aromatic Hydrocarbons.—Georges Darzens.—The reducing effect of the nickel depends upon how it has been prepared. It is more powerful when it is finely divided and when it has been prepared by reducing the oxide, NiO , at a low temperature. Thus aromatic ketones of the general formula $\text{C}_6\text{H}_5-\text{CO}-\text{R}$, hydrogenised by nickel which had been prepared at 300° , gave compounds having the formula $\text{C}_6\text{H}_5-\text{CH}_2-\text{R}$. But when nickel prepared at a much lower temperature was used, the corresponding hexahydro-derivatives were obtained.

No. 22, November 28, 1904.

Possibility of Chemical Reactions.—M. de Forcrand.—According to thermo-chemistry, a chemical reaction is possible if q (heat evolved) > 0 . According to thermodynamics, the condition of possibility is that $q - q' > 0$; where q' is a small correction which it is practically impossible to determine. Thus the thermo-chemical criterion is the only one of practical value. A similar paper follows, by the same author, on the prediction of chemical reactions.

The Colloidal State of Matter.—G. E. Malitano.—The author considers that matter in the colloidal state consists of an electrolyte dissociated into ions, and of insoluble molecules grouped round these ions.

MISCELLANEOUS.

King's College.—Department of General Pathology and Bacteriology.—Director: Professor Hewlett, M.D., M.R.C.P., D.P.H.; Demonstrator: H. S. Willson, B.A., M.B., D.P.H.

Examinations of the Institute of Chemistry.—Class in Bacteriology and Chemical Bacteriology for these Examinations. Candidates preparing for admission to the Intermediate Examination of the Institute may take Bacteriology as an optional subject. The course consists of demonstrations and practical work on two afternoons a week (or an equivalent amount) during one term (ten to twelve weeks). Subjects:—Nature of cells; the microscope and methods; general biology of bacteria; staining and culture methods; typhoid and *B. coli*; anthrax; tubercle; diphtheria; *B. enteritidis sporogenes*; bacteriological examination of milk and foods, air, water, and sewage; the yeasts and fermentation; moulds. The A.I.C. Examination.—The course for candidates preparing for the Final (A.I.C.) Examination in the Branch of Biological Chemistry consists of demonstrations and practical work two afternoons a week (or an equivalent amount) during two terms. Subjects:—As for the Intermediate, but treated more fully, and in addition enzymes, analysis of yeasts, fermentations, testing of filters, nitrification, certain chemical separations, e.g., indol, pigments, &c.

Evening Classes.—A course in practical and clinical bacteriology will be held every Monday evening (January to March) from 6.30 to 8.30, commencing January 9th. The course will consist of lectures, demonstrations, and practical work; in the latter, the members of the class will make for themselves permanent preparations of the chief pathogenic micro-organisms, and will carry out the usual manipulations employed in bacteriological investigations. Names should be sent in as soon as possible to the Secretary, or to Professor Hewlett, as the class will not be held if less than six students join. Syllabus:—Morphology and biology of the bacteria; the cultivation and isolation of organisms, culture media; anthrax; tubercle, tubercle of milk; diphtheria; typhoid and *B. coli*; anaerobic bacteria; principles of the bacteriological examination of water; fermentation. Practical Work:—Types of organisms, preparation of cover-glass specimens; cultures and plate cultivations; Gram's method; anthrax; tubercle; diphtheria; typhoid and *coli*; *B. enteritidis sporogenes*, &c.; examination of water; yeasts.

Decomposition of Carbon Dioxide under the Influence of Light.—A. Bach.—Euler has found that uranium acetate solutions are reduced in sunlight both in the absence of carbon dioxide and on passing nitrogen through them, but the author cannot obtain such reduction if carbon dioxide is absent, or if carbon dioxide is led through the solution in the dark. If, however, the carbon dioxide is introduced into the solution in direct sunlight, the uranium acetate is decomposed, giving a mixture of uranous and uranic hydroxides. Possibly these contradictory results are due to the presence of some foreign substance in one or other of the uranium acetate preparations employed.—*Berichte*, xxviii., No. 15.

The Part Played by Diaphragms in the Electrolysis of Saline Solutions.—W. Hittorf.—The different substances in general use as diaphragms play various rôles in electrolysis. Porcelain and agar-agar give rise to an electric endomose, such that the solution that remains undecomposed is only displaced in the direction of the positive current; on the other hand, intestinal membrane, as well as albumenoid substances and parchment paper, divide the solutions of several salts into a

more concentrated portion and a dilute portion; the former goes in the direction of the negative current, the latter in the positive direction, and both have a considerable speed. However, this phenomenon does not take place if the concentration of the solution reaches and passes a certain limit, which depends on the nature of the salt. All salts do not undergo this division; the alkaline salts behave, with these substances, in the same manner as they do with porcelain or agar-agar; they only give rise to a slight endomose, at a constant concentration, and in the direction of the positive current.—*Zeit. Physik. Chem.*, vol. xliii., p. 239.

Researches on Nitrifying Microbes.—E. Boullanger and L. Massol.—The authors have confirmed the fact that in nitrous fermentations we can replace the carbonate of ammonia with a carbonate of any other common base. The nitrification succeeds also with a large number of ammoniacal salts; it is slight with the arseniate, iodide, citrate, and oxalate, but proceeds very well with the borate and fluorhydrate; further, the nitric ferment oxidises nearly all the nitrites. It has been observed up to the present time that on sowing the nitrous and nitric ferments in an ammoniacal solution, the nitric fermentation begins only when the nitrous fermentation is completed. This phenomenon appears to be due to the action of the ammonia on the nitric ferment, of which it retards the reproduction, without interfering with its oxidising functions. Above 10 milligrams of ammonia per litre the retardation of the nitrification becomes marked. We see, moreover, that symbiosis is produced in the bacteria beds for the purification of waste waters; the formation of nitrites being so small. After having obtained a culture with the two microbes sowed simultaneously, we replace, aseptically, the exhausted liquid with an equal quantity of fresh broth; thus we obtain perfect symbiosis with a very slight production of nitrite; we may even obtain symbiosis at once by sowing the two ferments very copiously in the small rotating glass vessels described in a previous paper.—*Ann. de l'Inst. Pasteur*, vol. xviii., No. 3, pp. 181–196.

Abnormal Electrolysis.—P. Walden.—There is a large number of bodies, simple and compound, which without being either salts, acids, or bases, and consequently not capable of being looked upon as true electrolytes, are nevertheless, under many conditions, good conductors of the electric current; they appear to undergo electrolytic dissociation in a remarkable manner, which is shown by the energy and speed of the reactions to which they give rise when they are dissolved in certain ionising solvents; for example, liquid SO_2 , SO_2Cl_2 , AsCl_3 , &c. Of such a nature are the halogen elements in the free state; the compounds they form between themselves, their compounds with the metalloids, the tertiary bases of nitrogen, the carbinols, the carbides of hydrogen, the alcoholic bromides and iodides, and the acid chlorides and bromides. The author designates all these bodies by the name of "abnormal electrolytes," and has examined their electrolytic dissociation with a view to determining by measurements of their conductivity the nature of the ions they furnish. By this means he has arrived at the following conclusions:—1. The halogens (Br, I) give not only anions, but also cations, Br^- and Br^{++} , I^- and I^{++} . 2. The metalloids (P, As, Sb, Sn, S) also give cations, P^{++} and P^{+++} , As^{++} , Sb^{++} and Sb^{+++} , Sn^{++} , S_2^{++} . 3. The tertiary azotised bases (quinoline, pyridine, picoline) give bivalent cations, $(\text{RN})^{++}$. 4. Dimethylpyrone gives a bivalent cation, $(\text{C}_7\text{H}_5\text{O}_2)^{++}$. 5. The carbinols and the corresponding bromides and iodides give univalent cations, $(\text{C}_6\text{H}_5)_2\text{C}^+$. 6. The existence of acid cations, $(\text{CH}_3\text{CO})^+$, or PO^{++} , appears to be very probable.—*Zeit. Physik. Chem.*, vol. xliii., p. 385.

MEETINGS FOR THE WEEK.

TUESDAY, Jan. 3rd
THURSDAY, .. 5th
SATURDAY, .. 7th

Royal Institution, 3 (Christmas Lectures, adapted to a Juvenile Auditory). "Ancient and Modern Methods of Measuring Time" (Experimentally Illustrated), by Henry Cunningham, C.B., &c.

BIRKBECK COLLEGE,

Brems Buildings, Chancery Lane, E.C.

DAY AND EVENING SCIENCE CLASSES—

CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS.. .. .	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING	G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

Courses for University of London, Conjoint Board,
Dental, and Pharmaceutical Examinations.**PRACTICAL WORK** in highly equipped Laboratories.**SECOND EDITION.***With Illustrations.*

Price 2s. net (post free 2s. 1½d.)

Mdme. CURIE'S Thesis

ON

RADIO-ACTIVE SUBSTANCES.REPRINTED from the **CHEMICAL NEWS.****CONTENTS.**

Introduction.—Historical.—Chap. I. Radio-activity of Uranium and Thorium; Radio-active Minerals.—Chap. II. Method of Research.—Chap. III. Radiation of the New Radio-active Substances.—Chap. IV. Communication of Radio-activity to Substances Initially Inactive.—Nature and Cause of the Phenomena of Radio-activity.

16, NEWCASTLE ST., FARRINGTON ST., E.C.

ACETONE,

Chemically and Tech. pure.

METHYL-SPIRIT.**WOOD****NAPHTHA.****METHYLENE, Type Regis.****ACETON OIL.**

&c.

METHYLIC ALCOHOL

(Wood Spirit, Wood Naphtha).

MANUFACTURED BY

**Stora Kopparbergs Bergslags Aktiebolag,
FALUN (Sweden).****SILICATES OF SODA AND POTASH.**IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION
FULL STRENGTH GUARANTEED.**OLDEST AND MOST RELIABLE MAKE***Supplied on best terms by***WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.**LONDON AGENTS—CLIFFORD CHRISTOPHERSON & CO.,
21, Mincing Lane, London, E.C., who hold stock ready for delivery.**RECTIFIED SPIRIT**

(SPIRITS OF WINE).

B.P. and higher strengths. Duty paid; or
Duty Free under Finance Act 1902.**METHYLATED SPIRIT****Special Quotations to large
Institutions.****BOORD & SON,**

DISTILLERS SINCE 1750,

115-121 Tooley Street,

LONDON, S.E.

BRYAN CORCORAN LIM.**MILLSTONE BUILDERS,
WIRE WEAVERS, MACHINE MANUFACTURERS AND
GENERAL MILL FURNISHERS.**Sole Makers of MILBURN'S
Patent Coroidal Stone Grinding Mills.
Especially suitable for certain materials, Wet or Dry.Works and Warehouses: Back Church Lane,
Faversham Dept.: Basement of the Corn Exchange,
31, MARK LANE, LONDON.**E. GEORGE & SONS,**

BOOKSELLERS,

151, WHITECHAPEL ROAD, LONDON, E.,

Are OPEN to PURCHASE Complete Sets
or short runs of the following:—*Chemical News, The Analyst
Journal of the Chemical Society, 1848 to 1870, Journal of the Society
of Chemical Industry, or the Publications of any other English or
Foreign Learned and Scientific Societies.—Libraries Purchased.*
Current Catalogue of General Literature sent on application.

**OLD PLATINUM**

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver
Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and Purchased.

COVERS FOR BINDING.Cloth, Gilt-lettered Covers for Binding the Half-yearly
Volumes of the**CHEMICAL NEWS**

may now be obtained. Price 1/6 each (post free 1/8).

Volumes Bound in Cloth Cases, Lettered, and Numbered
at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGTON ST., E.C.

REDRUTH**SCHOOL OF MINES.****School Re-opens Jan. 4th,
1905.***Syllabus on application to—*

THE REGISTRAR.

Chemische Fabrik Eidelstedt,

Joh. Oswaldowski, Altona E.

INDEX.

- A**BEL, Sir F., and W. R. Dunstan. (See Dunstan, W. R.)
 Aberdeen University, 131
 Aberystwyth, University College of Wales, 124
 Acetamide, transformation of aceto-homocine into, 7
 Acetates, glucosidic, hydrolysis, 32
 Acetyl oxidation, 293
 Acetone, condensation of formaldehyde with, 255
 hydration, formation of dimethylisopropylcarbinol during, 45
 in urine, detection, 148
 Acetones, β -oxal-, α - and β -oxyphenol ethylenic, 117
 Acetophenone, transformation into acetanilide, 7
 Acetyl chloride, action on sodium salt of diacetylacetone, 19
 groups, determination, 32
 Acetylacetone, 19
 Acetylides, double, 140
 Acid, adipic, preparation, 10
 secondary products of, 10
 amygdalinic, fractional hydrolysis, 276
 bismuthopyrocatechuic, 244
 boric, action on alkaline peroxides, 304
 bromobutyric, β -, 293
 bromopivalic, and derivatives, 244
 brom-succinic and its salts, products of decomposition in aqueous solution, 94
 carbonic, action on phenylbromide of magnesium, 247
 electrolytic reduction, 161
 chloric, determination, 325
 dimethyladipic, α -, synthesis, 70
 dimethyladipic, $\beta\beta$ -, synthesis, 304
 dimethylpyroarsinic, 148
 dyes, action on wool fibres, 233
 galic, estimation, 111
 glyoxylic, history of, 253
 hydrobromic, action on triacetin, 328
 hydrochloric, action on platinum and gold, 10
 on triacetin, 328
 hydrosulphuric and the inorganic trinitrides, 272, 287, 298, 317, 321
 preparation from sodium trinitride, 312
 hydroxylauric, 35
 hypophosphorous, phosphorus derivatives, 57
 lactic, action of fermentation, decomposition, 70
 lauric, derivatives, 35
 metanitrobenzoic, separation of thorium from cerium, lanthanum, and didymium by, 196, 201
 nitric and ethers, compounds, 265
 nitrous, action on monophenylurea, 234
 oleic, 278
 oxalic, behaviour of chromic hydroxide towards, 254
 oxypivalic, 148
 peroxylamine sulphonic, 42, 69
 persulphuric, Caro's, and hydrogen peroxide mixtures, effect of chloridic platinum on, 262
 phenylazoisovaleric, β -, 290
 phenylhydrazidobutyric, α -, 290
 phosphoric, derivatives of pentabasic, 143
 phosphoric, estimation, ponderable or gasometric, 161
 pimelic, synthesis, 63
 sorbic, conversion into aminoacids, 46
 sulphuric, electrolysis of concentrated, 26
 in concentrated solution, molecular condition, 253
 solutions, vapour pressures, 253
 tannic, estimation, 111
 thioformic, 304
 vinylidimethylacetic, 117
 Acids, alkyl sulphonic, preparation, 45
 conversion of sorbic acid into, 46
 and salts, superoxygenated, in solution, 11
 aromatic, in phenol solution, chlorobromobenzoic, rotation of the menthyl esters of the isomeric, 251
 chromogamic, 254
 crotonic, isomerism of α - and β -, 166, 264
 dialcylhydracrylic, 148
 iodoobenzoic, rotation of menthyl esters of isomeric, 252
 nitrobenzoylauric, methyl and ethyl esters of di- α , α -, α -, and β -, 277
 of ethylene series, action of iodine and yellow oxide of mercury on, 328
 organic, converting into esters, 256
 oxymethylene, and bismuth, compounds, 57
 Acrotyl, bearing of colour phenomena presented by, 157
 Acridines, halides of, 251
 Actinium, 232
 Acylaminoketones, isomeric change of diacylanilides into, 291
 Adrenaline, chemical composition, 207
 Aeuer, E., and P. Kothner. (See Kothner, P.)
 Air and volatile gases, separation without liquefaction, 90
 Albumen, 194
 "Albuminous Substances, Chemistry of" (review), 82
 Alchemy, 161
 Alcohol, campholenic, isomer of, 244
 duty-free for industrial purposes, 145
 nitrobenzyl-, α -, reduction, 37
 Alcohols, ethyl and methyl, oxidation at boiling-points, 281
 in cyclohexane series, synthesis, 118
 tertiary, from cyclohexanol, synthesis, 10
 univalent, action of isocyanate of phenyl on, 58, 70
 Aldehydes, formic, formation in combustion of tobacco, 281
 in products of combustion and smoke, 45
 hexahydrobenzoic, 11
 Aldehydes, acetylenic, 10
 aromatic, action of oxalacetic ether on, 117
 "Alkali, &c., Works, Annual Report on" (review), 147
 "Alkali Metals, Electro-metallurgy of the" (review), 9
 Alkali metals, nitrates of, and decomposition by heat, 301
 Alkaline earths, attempt to explain the occurrence of zinc, cadmium, and mercury in the same group with, 271
 nitrates of, and decomposition by heat, 301
 metals, attempt to explain the occurrence of copper, silver, and gold in the same group with, 271
 peroxides, action of boric acid on, 304
 Alkalis and bisulphide, double hypsulphites of, 71
 caustic, action on diphenylcarbinol ether, 83
 "Alkaloids, Vegetable" (review), 31
 Alkyl groups, removal from secondary amines, 118
 halogen compounds, action of halogen derivatives of tri- and pentaerythritol on, 269
 Allan, G. R., note on the properties of lenses, 243
 Alloys, magnetic, production from iron, 219
 steel-making, determination of molybdenum in, 204, 218
 Alternator, high-frequency, 315
 Alumina in aluminum powder, 6
 Aluminium and antimony alloys, 45
 and bismuth alloys, 35
 and magnesium alloys, 35, 45
 atomic weight, 280
 powder, 5
 oxidation, 7
 suggested new source, 232
 American Institute of Electrical Engineers, Report of Committee on Cadmium Cell, 225
 Amers, application of, 263
 Amidides of the naphthalene series, isomerism, 288
 Amidochloroiodides, 290
 Amines, aromatic, condensation with aniline benzylidene, 45
 constitution, determination, 269
 primary, secondary, and tertiary, differentiation, 31
 decomposition, removal of alkyl groups from, 118
 Aminocoumarin, 6-, 251
 Ammonia, action on boron bromide and phosphorus chloride, 118
 and salts of metals, compounds, 107
 decomposition and synthesis, 182
 by heat, 113
 gas, action on arsenic trichloride, tribromide, and triiodide, 70
 Ammonised compounds, constitution, determination, 269
 Ammonium compounds, constitution, 39, 52
 salts and metals, reactions between, 142
 Amygdalin, 180-276
 "Analysis, Elementary, Percentage Tables for" (review), 255
 "Analysis, Qualitative Chemical, Tables for" (review), 254
 "Analysis, Quantitative Chemical, Text-book of" (review), 268
 "Analysis, Quantitative, for Mining Engineers" (review), 9
 Analysis, approximate harmonic, 215
 electrolytic, use of complex salt in, 215
 Analysis, gasometric, use of sulphate of hydrazine in, 247
 of organic compounds, 250
 qualitative, determining presence of an oxide, 33
 Andrews, L. W., new method for preparation of pure iodine, 27
 Anhydride, carbonic, action of, 57
 phthalic, action on magnesium α -naphthyl bromide, 276
 sulphurous, density, 82
 Anhydrides, effect on organo-magnesium bromides, 276
 Anilides, preparation, 24
 Aniline and its derivatives, affinity constants of, 302
 Anthracene series, synthesis in, tetrahydride and octahydride of, 256
 Antimony, action of magnesium alkyl compounds upon the halogen derivatives of, 255
 and aluminium alloys, 45
 and copper separation, 215
 sulphide, a lenticular form of, 70
 trisulphides, heat of formation, 256
 "Apparatus, Physical, Catalogue of" (review), 245
 Apparatus exhibition, 267
 for determination of curvatures of small lenses, 279
 interference, for calibration of extensometers, 244
 Kipp's, 154, 286
 Argon, beryllium, and tellurium, atomic weights, irregularities of, 261
 Aries, E., theory of diuile solutions based on van't Hoff's law, 148
 Armstrong, E. P., and P. S. Arup, stereoisomeric glucoses and the hydrolysis of glucosidic acetates, 32
 H. E., retardation of combustion by oxygen, 25
 Arnold, C., and J. A. Mandel, "Compendium of Chemistry" (review), 81
 Arnold, J. O., notes on the fracture of structural steel under alternating stresses, 211
 "Aromatic Substances" (review), 44
 Arsenic, action of magnesium alkyl compounds upon halogen derivatives of, 255
 and copper separation, 215
 separation by distillation in hydrogen chloride, 31
 trichloride, tribromide, and triiodide, action of ammonia gas on, 70
 Arth, G., and P. Ferry, purification of natural mineral waters, 11
 Arup, P. S., and E. F. Armstrong. (See Armstrong, E. F.)
 Aschan, O., pentavalent nitrogen atom, 192
 Ashby, S. F., comparative nitriding power of soils, 250
 Ashley, H. E., silica determinations, 274
 Asphalt, 185
 Atkinson, G. A. S., and E. P. Ferman. (See Ferman, E. P.)
 Atom, nitrogen, pentavalent, 192
 "Atomic Weight, Relations between Equivalent Volume and" (review), 116
 Atomic weights, international table of, 28
 of beryllium, argon, and tellurium, irregularities of, 260

- Auger, V., action of acid chlorides on tetracyclic bases having an aromatic radical, 17
of halogen derivatives of the tri- and penta-valent metalloids upon alkyl halogen compounds, 269
methyl arsenic, 57
new method of preparing organic derivatives of phosphorus, 269
thioacetic acid, 374
and M. Billy, action of magnesium alkyl compounds upon halogen derivatives of phosphorus, arsenic, and antimony, 253
Austin, P. C., and A. Senier. (See Senier, A.)
Australian minerals, radium in, 250
Auerth, W., microchemical detection of strontium and the properties of strontium chromate, 305
"Autoxidation, Critical Studies on the Processes of" (review), 173
BACH, A., decomposition of carbon dioxide under the influence of light, 329
Balfour, Right Hon. A. J., reflections suggested by new theory of matter, 25
Bal, C. C. G., and C. H. Desch, ultra-violet absorption spectra of certain enol-tautomers, 19
Bangor, University College of North Wales, 124
Barger, G., saponario, 183
Barium carbonate, purification of mineral matters by, 11
Baron, H., F. G. P. Kempf, and J. F. Thorpe, formation and reactions of imino compounds, 301
Bases, tertiary, products obtained by action on acid chlorides, 152
Baskerville, C., thorium, carolinium, berzelium, 151, 163
Bateson, W., Darwin Medal, 250
Battersea Polytechnic, 135
Baud, E., dimethylpyrosulphuric acid, 148
Beard, S. H., H. Hibbert, and J. J. Sudborough. (See Sudborough, J. J.)
Becker, F. E., and Co., "Catalogue of Physical Apparatus, &c." (review), 245
gummed reagent labels, 249
11, "Die Elektrolyturgie der Alkalimetalle" (review), 9
Beckmann rearrangement, 7
Bequerel, H., use of N-rays in chemistry, 11
Behal, A., isomer of borneol, campholenic alcohol, and some camphenolic derivatives, 249
and M. Tiffeneau, certain phenolic ethers with pseudo-allylic chain, 52
Beilby, G. I., action of certain gases on glass in the neighbourhood of heated metals, 180
relation between the crystalline and the amorphous states as disclosed by the surface flow of solids, 141
Beis, C., action of mixed organo-magnesium compounds on phthalimide and phenyl phthalimide, 70
Beismenger, A., and H. Kauffmann. (See Kauffmann, H.)
Belast, Queen's College, 133
Bell, Sir Lewis Lowman (obituary), 316
Bell, A. E., and R. S. Morrell. (See Morrell, R. S.)
Benedicks, C., "Recherches Physiques et Physico-chimiques sur l'Acier au Carbone" (review), 51
Benedict, S. R., some methods for the detection of cobalt and nickel, 109
Benzaldehydes, condensation products with ketones, 277
Benzene derivatives and radium rays, 216
ring system of, 208
series, hydrocarbons of, electro-lytic oxidation, 232
Benzophenone, transformation into triphenylcarbinol, 36
Benzopinacolone, 107
Benzopinacolone, 107
a-Benzoyl- β -trimethylacetylstyrene, 277
Benzylidenacetophenone, addition of hydrogen cyanide to, 253
Berger, E., basic ferric phosphate, 34
"Birmingham Technical High School, Royal Testing Office of the" (review), 146
Berries, sorb, sugar from, 304
Berthelot, M., chemical effects of light on hydrogen cyanide and its action on potassium cyanide, 56
solubility and polymerisation, 50
chemical investigations on solution and polymerisation of cyanogen, 82
Bertaux, L., and A. Hoillard. (See Hoillard, A.)
Bernard, G., chemical composition of cyanide, 207
new sugar from sorb berries, 304
P., and K. Fosse. (See Fosse, K.)
Beryl, composition, 263
Beryllium. (See Beryllium)
Berzelium, 151, 163
Bettings, W., and P. Jannasch. (See Jannasch, P.)
Beyer, H. O., radium, 250
Biddle, H. G., and A. Pictet. (See Pictet, A.)
Billy, M., and V. Auger. (See Auger, V.)
Birkbeck College, 135
Birmingham University, 126
Bischoff, C. A., "Die Materialien der Stereochemie" (review), 116
Bismuth and alkalis, double hypsulphites of, 71
and aluminum alloys, 35
and oxygenized alloys, compounds, 57
estimation by electrolysis, 118
pyrophosphoric, 118
phosphite and meta-ate, 143
Buckham Municipal Technical School, 136
Blaise, E. E., preparation of glutacate of ethyl, 10
and A. Courtot, vinylidimethylacetic acid, 117
and H. Gault, researches in the pyrene series, 82
and L. Marclay, β -aldehyde bromide, 244
a-allyl, allyl, and diacetyl acids, 148
Blanc, G., new synthesis of a-dimethylaldehyde, 70
of β -dimethylaldehyde acid, 304
Bloch, A., action of isocyanate of phenyl on some univalent alcohols, 58, 70
Bloxam, W. F., our present knowledge of the chemistry of indigo, 19
Blue, Prussian, estimation, 78
Bodenstein, M., and W. Ostwald. (See Ostwald, W.)
Bodrus, F., new method of preparation of antides, 24
organo-magnesium derivatives of the di-halogen aromatic hydrocarbons in the radical, 107
Boiling-point constants of mixtures, 255
Bolton, H. C., "Select Bibliography of Chemistry, 1492-1902" (review), 327
Bone, W. A., and R. V. Wheeler, combustion of ethylene, 276
Book Circular, International, 305
Borchers, W., "Die Beziehungen Zwischen Äquivalent-volumen und Atomgewicht" (review), 116
Bornol isomer, 244
Boron bromide, action of ammonia on, 118
Borough Polytechnic Institute, 135
Boudouard, O., alloys of zinc and magnesium, 160
Bougault, J., action of iodine and yellow oxide of mercury upon acetylene, 325
Boulanger, E., and L. Massol, researches on nitrifying microbes, 329
examination of nitrifying microbes, 11
Bouveault, L., action of oxygen on organo-halogen-magnesian derivatives, 11
hexahydrobenzoic aldehyde, hexahydrobenzoic anhydride, and the corresponding secondary alcohol, 11
preparation of adipic acid, 10
rhodamine, 10
secondary products of electro-lytic preparation of adipic acid, 10
and M. Gourmand, total synthesis of rhodolol, 57
and A. Wahl, reactions of α -diketo-butyric ethers, 82
Brachin, M., and C. Moureu. (See Moureu, C.)
Bradford City Technical College, 135
Bran, wheat, nature of principal phosphorus compound in, 112
Bredig, G., and G. von Schukowsky, examination of liquid crystals by means of electrical capillarity, 244
Brenans, P., iodine compounds obtained with meta-nitrilamine, 35, 70
Brissle, F. J., potential of the hydrogen electrode, 293
Briston, Merchant Venturers' Technical College, 126
University College, 125
"British Journal of Photography" (review), 2
British Association, 58, 71
Chemical Section Address, 97
Presidential Address, 85
Section B, 118
Science Guild, 80
Brixton School of Chemistry and Pharmacy, 135
Brochet, A., and J. Petit, electrolysis of cyanides, 321
electrolytic solution of platinum, 310
influence of frequency on electrolysis by means of alternating currents, 23
of the nature of the anode upon the electrolytic oxidation of potassium ferrocyanide, 328
Bromates, estimation, use of ferrous sulphate in, 195
Bromides, organo-magnesium, effect on anhydrides on, 276
Bromine, electric conductivity of solutions in, 269
Brown, A. W., and L. M. Dennis. (See Dennis, L. M.)
Bruce, Colonel D., Royal Medal, 250
Brubi, J. W., researches in the camphor group, 46
Bunsen, Robert, "Collected Works of" (review), 146
Burgess, C. H., and D. L. Chapman, active chlorine, 170
photochemically active chlorine, 21
and A. Holt, jun., some physical characters of sodium borates, 254, 296
H. E., improved form of condenser, 249
Burgess, H. E., and T. H. Page, note on bergamot oil and other oils of citrus series, 252
Burnside, W., Royal Medal, 250
Burt, B. C., vapour pressures of sulphuric acid solutions and the molecular condition of sulphuric acid in concentrated solution, 253
Butea frondosa flowers, colouring matter of, 32
Butterfield, W. A., "Chemistry of Gas Manufacture" (review), 327
CADMIUM Cell, Report of Committee on, 225
occurrence in same group with the alkaline earths, 271
Cain, J. C., constitution of the ammonium compounds, 39, 52
Calcium carbonate and alkaline carbonate, decomposition of a mixture, 34
Caldecott, W. A., influence of sunlight on the dissolution of gold in aqueous potassium cyanide, 275
Calorimetric determinations, 269
Cambridge University, 122
Cameron, A., and J. C. Irvine. (See Irvine, J. C.)
Campagne, E., volumetric estimation of vanadium and chromium in solution together, 237
Camphenolic derivatives, 244
Camphor derivatives, action of magnesium alkyl halides on, 278
group, researches in, 46
Canon Diabolo, 295
Cantoni, H., and G. Goguel, decomposition of alkaline-earth carbonates by chloride of ammonium in presence of water, 1
Cantor, G., Sylvester Medal, 250
Caoutchouc, varieties, 34
Caprolactone, iso-, and derivatives, synthesis, 290
Carbides and cyclohexanones, 221
Carbohydrates, action of H_2O_2 on in presence of ferrous sulphate, 158
"Carbon Compounds, Scheme for Detection of more Common Classes of the" (review), 268
Carbon compounds, reactions involving the addition of hydrogen cyanide to, 251
dioxide, decomposition under influence of light, 329
estimation by oxidation with chromic acid, 31
group, attempt to explain occurrence of tin and lead in, 271
steels, cementation, 44
Carbonates, alkaline-earth, decomposition, 44
phenolic, action of secondary bases on, 57
Carcano, L., and R. Namias. (See Namias, R.)
Cardiff, University College of South Wales and Monmouthshire, 125
Caro's persulphuric acid and hydrogen peroxide mixtures, effect of colloidal platinum on, 269
Carolinium, 151, 163
Carpenters' Company Technical Institute, 136
Carré, F., new anhydride of dulcitate, 269
Cartaud, G., evolution of structure in metals, 160
and F. Osmond. (See Osmond, F.)
Carré, 194
"Catalogue of Physical Apparatus, &c." (review), 245
Catechins, 32
Cavalier, J., acid silver pyrophosphate, 117
Cement, hydraulic, 184

- Cements, silicate and oxy-chloride, 194
- Cellulose and its nitrated derivatives, optical activity, 148
- Centnerswer, M., and F. Walden. (See Walden, F.)
- Cerium and thorium, separation by metanitrobenzoic acid, 195, 201
- Chapman, D. L., and C. H. Burgess. (See Burgess, C. H.)
- Charabot, E., and G. Laloue, production and distribution of some organic substances in the mandarin orange tree, 244
- Charcoal, absorption of gases by, 109
- condensation of helium and hydrogen by, 145
- Charpy, G., and L. Grenet, transition temperatures of steels, 243
- Chattaway, F. D., nitrogen chlorides containing two halogen atoms attached to the nitrogen, 31
- sulphonoalkylamines, 278
- sulphophenylchloroamides and sulphothioylchloroamides, 32
- and W. H. H. H., isomeric change of diacylanilides into acylaminoketones, 291
- Chelmsford County Technical Laboratories, 136
- Chelsea, South-Western Polytechnic, 135
- "Chemical Conception of the Ether" (review), 326
- "Chemical Examination of Technical Products" (review), 116
- "Chemical Novelties for 1904" (review), 22
- "Chemical Synthesis of Vital Products and the Inter-relationships of Organic Compounds" (review), 221
- "Chemical Technology and Analysis of Oils, Fats, and Waxes" (review), 197
- Chemical action and gravity, 53
- constitution, relation of crystal structure to, 142
- literature, abstracting, 283
- reactions, possibility of, 328
- water, natural, 107
- Society, 17, 31, 250, 262, 275, 288, 300
- Research Fund, 270
- "Chemistry, Applied" (review), 116
- "Chemistry, Compendium of" (review), 31
- "Chemistry, Elements of" (review), 33
- "Chemistry, Inorganic, Elements of" (review), 207
- "Chemistry of Albuminous Substances" (review), 32
- "Chemistry, Physiological, Directions for Laboratory Work" (review), 9
- "Chemistry, Physical, Elementary Treatise on" (review), 327
- "Chemistry, Physical, Introduction to" (review), 68
- "Chemistry, Physiological and Pathological, Laboratory Manual of" (review), 9
- "Chemistry, Practical" (review), 145
- "Chemistry, Select Bibliography of, 1892-1893" (review), 327
- Chemistry and Physics, Handbook on, 24
- Nobel Prize for, 300
- organic, present problems of, 212, 228
- "Chemists and Druggists, Kelly's Directory of" (review), 24
- Chloral hydrate decomposition by sodium hydroxide and by certain salts, 253
- Chlorates, estimation, use of ferrous sulphate in, 105
- Chlorides, acid, action on tertiary bases having an aromatic radicle, 117
- Chlorides acid, products obtained by action of tertiary bases on, 124
- diacetic, action on oxalacetic ethers, 70
- in alkaline solution, action on oxalacetic ether, 70
- metallic, and unsaturated ketones, compounds, 257
- Chlorine, active, 170
- and hydrogen, union, 265
- gaseous, decay of activity of, 265
- photochemically active, 21
- Chloroform, boiling-point of, influence of moist alcohol and ethyl chloride on, 21
- Chlorophyll spectrum, 291
- Chretien and Guinchaut, MM.
- Chromates of polyatomic metals, 95
- Chromium and vanadium in solution together, volumetric estimation, 137
- in steel, determination, 320
- steels, preparation and properties, 160
- Chromyl chloride, action on stilbene, stilbene, and phenanthrene, 252
- Cinnabarytes, radio-active, 217
- Cirencester, Royal Agricultural College, 127
- Clarke, G., international atomic weights, 56
- G. jun., and W. J. Pope. (See Pope, W. J.)
- Clay, 184
- Cobalt electrolyte, electrolytic, 307
- Cobalt, B. G., phenomena observed during the electrolysis of concentrated sulphuric acid, 26
- Cohn, A., and S. Jahn, electrochemical reduction of carbonic acid, 161
- Coffmeyer, C., method for the estimation of Prussian blue, 75
- Cohen, J. B., and H. D. Dakin, chlorination of the trichlorotoluenes in presence of the aluminium-mercury couple, 252
- and J. Gatecliffe, basic properties of oxygen, compounds of ethers with, 212, 245
- and J. Miller, influence of substitution in the nucleus on rate of oxidation of side chain, 290
- and H. S. Raper, relation of position isomerism to optical activity, 251
- Cohn, G., "Die Reichstoffe" (review), 44
- Cobnheim, O., "Chemie der Eiweisskörper" (review), 82
- Coke, absorption of gases by, 109
- Collie, J. N., action of diacetyl chloride on sodium salt of diacetic acid, constitution of pyrene compounds, 19
- method for the rapid ultimate analysis of certain organic compounds, 250
- methyl fluoride, 122
- Colloidal state of matter, 320
- Colouring matter of flowers of Butea frondosa, 32
- matters of stilbene group, 253, 316
- Combustion products, formic aldehyde in, 45
- retardation by oxygen, 25
- Compounds, olefinic ketonic, action of organic bases on, 182
- Condenser, improved form of, 249
- Conduche, A., and L. J. Simon. (See Simon, L. J.)
- Conductivity, electrical, and chemical dissociation, 21
- Cone, L. H., and M. Gomberg. (See Gomberg, M.)
- Conte, A. H., and W. R. Hodgkinson. (See Hodgkinson, W. R.)
- Copley, R. D., 250, 303
- Copper and antimony separation, 215
- Copper and arsenic separation, 215
- in same group with the alkaline metals, attempt to explain, 274
- Corbin and Stewart's Handbook on Physics and Chemistry, 24
- Cork, Queen's College, 134
- Courtois, A., and E. E. Blaise. (See Blaise, E. E.)
- Craig, G., absorption of gases by charcoal and coke, 109
- Crepieux, P., and F. Reverdin. (See Reverdin, F.)
- Crookes, Sir W., action of radium emanations on diamond, 1
- Copley Medal, 250, 303
- and Sir J. Dewar, London water supply, 43, 106, 172, 201, 262, 314
- Crosley, A. W., dihydrobenzene, 20
- study of hydro-aromatic substances, 168
- and Nora Renouf, synthesis of 1:1-dimethylhexahydrobenzene, 301
- Crucible lid, improved form, 318
- Cruser, F. van D., and E. H. Miller, determination of molybdenum in steel and steel-making alloys, 204, 218
- Cryoscopy, comparative, 291
- Crystal structure and its relation to chemical constitution, 142
- "Crystals, Liquid" (review), 117
- "Crystals, attractive force for like molecules in saturated solutions, 302
- liquid, examination by means of electrical cataphoresis, 144
- showing the phenomenon of luminous rings, 279
- Crystalline and amorphous states, relation between, 141
- Cupels, magnesia, 23
- Cuthbertson, C., refractive indices of the elements, 272
- Cyanides, electrolysis, 321
- Cyanogen, action on potassium cyanide, 56
- solubility and polymerisation, 56
- solution and polymerisation, 82
- Cyanohydrins regarded as complex acids, 251
- Cyanogen, action on, 251
- Cyclohexanones, 221
- Cyclohexanol, synthesis of tertiary alcohols from, 10
- DAKIN, H. D., fractional hydrolysis of amygdalonic acid, isomaygdalin, 276
- and J. B. Cohen. (See Cohen, J. B.)
- Dannehl, H., "Jahrbuch der Elektrochemie" (review), 69
- Darwin Medal, 250
- Darzens, G., action of reduced nickel upon aromatic ketones, 328
- David, T. W. E., and F. B. Guthrie. (See Guthrie, F. B.)
- Davis, F., preliminary notes upon Seignette's crystallization, 2
- O. C. M., and F. E. Francis. (See Francis, F. E.)
- R. O. E., analysis of kunzite, 80
- Davy Medal, 250, 303
- De Bruyn, C. A. L., and C. H. Sluiter, Beckmann rearrangement, 7
- De Forcrand, M., possibility of chemical reactions, 328
- De Girard, J., and A. de Saporta, use of sulphate of hydrazine in gasometric analysis, 247
- De Gramont, M. le Comte A., characteristic sulphur lines in the photographic spectroscopy of minerals, 140
- observations on the grouping of lines in silicon spectrum, 156
- De Koningh, L., note on urine of tortoise, 64
- De Lacerda, H., action of hydrobromic and hydrochloric acids on triacetin, 328
- De la Roche, M. Houcheta, action of secondary bases on phenolic carbonates, 57
- De Saporta, A., and J. de Girard. (See De Girard, J.)
- De Watteville, C., flame spectra, 13
- Dean, G., bromination of silver cyanide, 253
- Deberrie, A., actinium, 232
- radio-active lead, radio-tellurium, and polonium, 92
- Debourdeaux, L., modifications of procedure in estimating nitric nitrogen by the Pelouze-Fresenius method, 57
- Debus, H., contributions to history of glyoxylic acid, 253
- Delange, R., transformation of benzophenone into triphenylcarbinol, 36
- two homologues of pyrocatechin, 57
- and C. Moureu. (See Moureu, C.)
- Denigès, G., formation of dimethylisopropylcarbinol during hydration of acetone, 45
- Denk, B., and A. Stahler. (See Stahler, A.)
- Dennis, M., and A. W. Brauer, hydronic acid and the inorganic trinitrides, 272, 277, 298, 311, 321
- Desch, C. H., and E. C. Baly. (See Baly, E. C.)
- Descube, M., new class of ether oxides, 57
- "Destructors, Small, for Institutional and Trade Waste" (review), 243
- Dewar, Sir J., absorption and thermal evolution of gases occluded in charcoal at low temperatures, 73
- condensation of helium and hydrogen by charcoal, 145
- Gunning Victoria Jubilee Prize, 281
- new low temperature phenomena and their scientific applications, 141
- separation of the most volatile gases from air without liquefaction, 90
- Lavoisier Gold Medal, 305
- and W. Crookes. (See Crookes, Sir W.)
- Diacylacetone, sodium salt of, action of acetyl chloride on, 19
- Diacylanilides, isomeric change into acylaminoketones, 291
- Diamond, action of radium emanations on, 1
- Diaphragms, part played by in electrolysis of saline solutions, 129
- Diazo-amido-compounds, latic aromatic, 83
- Diazo-benzene chloride, action on, 24
- Di-bromopentane, 45
- Didymium and thorium, separation by metanitrobenzoic acid, 195, 201
- Dietrich, C., energy of water and steam at high temperatures, 139
- Digliculose, presence in kinos of Eucalypts, 63
- Dihydro-methylindole, resolution externally compensated, 253
- Dihydrobenzene, 20
- Di-isopentane, 45
- Dimethylhydrazinobenzil, 1
- Dimethylhydrazinobenzil, 1
- Dimethylhexahydrobenzene-1:1, 1
- synthesis, 301
- Dimethylisopropylcarbinol, formation during hydration of acetone, 45
- Dimaphthol 2-2, azonic dyes derived from, 45
- "Directory of Chemists and Druggists, Kelly's" (review), 24
- Dissection, chemical, and electrical conductivity 21
- electrolytic, 292

- Dite, A., formation of vanadium ores in nature, 10
 Divers, E., constitution of nitric peroxide, 65
 peroxylaminesulphonic acid, 22, 69
 Dobbie, J. J., and C. K. Tinkler, constitution of hydrastinine, 20
 Doht, R., and J. Haeger, action of nitrous acid on monophenylurea, 224
 Donat, F. G., suggested explanation of phenomena of pale-escence observed in neighbourhood of critical states, 139
 Dourlein, J., and K. Duchemin. (See Duchemin, R.)
 Dreaper, W. F., effect of mercerising on dye-affinity, 179
 estimation of tannic and gallic acids, 111
 notes on gravity and chemical action, 53
 technical research and the college system, 2
 "Druggists and Chemists, Kelly's Directory of" (review), 24
 Drysdale, C. V., apparatus for determination of curvatures of small lenses, 279
 curvature-method of teaching geometrical optics, 279
 Duddell, G. Royal College of Science, 134
 Royal Society, 33
 University, 122
 Dubreuil, L., action of pyridine and quinoline bases upon bromo-succinic and dibromo-succinic ethers, 328
 Ducca, W., and K. A. Hofmann. (See Hofmann, K. A.)
 Duchemin, R., and J. Dourlein, oxidation of methyl and ethyl alcohols at boiling-points, 281
 Duddell, W., high-frequency alternator, 315
 Duluth, N. Y., 259
 Dundee, University College, 131
 Dunstan, W. R., and Sir F. Abel, "Imperial Institute, Technical Reports and Scientific Papers" (review), 254
 Durham College of Science, Newcastle-on-Tyne, 129
 Dye affinity, effect of mercerising on, 179
 Dyes, acid, action on wool fibres, 233
 azoic, derived from 2,2-dianaphthol, 45
 effect of low temperature on, 293
 theory of, 328
 Dyke, G. B., practical determination of mean spherical candle power of incandescent and arc lamps, 266
- EARTHS**, alkaline, nitrates of, and decomposition by heat, 501
 rare, serial order of, 310
 Edinburgh, Heriot-Watt College, 132
 University of, 132
 Edwards, Major A. E., and Prof. W. R. Hodgkinson, double acetylides, 140
 "Electric Furnace" (review), 245
 "Electrochemical Annual" (review), 69
 "Electrochemical Industry of Germany" (review), 116
 "Electro-chemistry" (review), 159
 Electrode in stationary liquids, measurement of potential of, 231
 Electrolysis, abnormal, 329
 b) alternating currents, influence of frequency on, 23
 Elements, properties of, changes induced in by viewing them under other external conditions than those common in the laboratory, 189
 representing graphically by means of characteristic surfaces, 175
- Elements, refractive indices of, 272
 Emulsion, 259
 Emmerling, O., origin of fusel oils, 256
 Energy, thermochemical, transformation into voltaic energy or electro-motive force, 41
 "Engineers, Mining, Quantitative Analysis for" (review), 9
 Engler, C., and J. Weissberg, Kritische Studien über die Vorgänge der Autoxydation" (review), 173
 Enol - ketotautomerides, ultra-violet absorption spectra, 19
 Epichlorhydrin, action of organo-magnesium derivatives, 57
 "Equivalent Volume and Atomic Weight, Relations between" (review), 116
 Erdmann, E., oxidation products of phenylamine, 121
 H., and O. Makowska, determination of palladium, 69
 Esters, aromatic, electrolytic reduction, 257
 converting organic acids into, methyl and ethyl, of di-o-, m-, and p-nitrobenzoyl tartaric acids, 277
 of hydroxy-acids, Grignard reaction applied to, 302
 Estragal and aromatic derivatives, synthesis with non-saturated chain, 181
 "Ether, Chemical Conception of the" (review), 32
 Ether, diphenylcarbonic, action of salts and caustic alkalis on, 83
 ovalaccatic, action of diazoic chlorides in excess in alkaline solution on, 70
 on aromatic aldehydes, 117
 product of spontaneous alteration of, new class of, 57
 Ethers, β -aldehydic, 244
 allylic, of borneol, menthol, methylcyclohexanol, and linalol, 56
 and sulfuric acid compounds, 265
 bromo-succinic and dibromo-succinic, action of pyridine and quinoline bases on, 328
 α -diketobutyric, reactions of, 8
 oxalaccatic, action of diazoic chlorides on, 70
 oxyformic, action of chloride of diazobenzene on substituted, 71
 phenolic, with pseudo-allylic chain, 82
 Etherification, Williamson's theory, 23, 44
 Ethyl acetate, 19
 cyanoacetate, condensation with its sodium derivative, 301
 gluconate, preparation, 10
 Ethylene, combustion, 276
 iodide, decomposition under influence of iodine ion, 297
 Eucalypta, kinds of, absence of gum and presence of diglucose, 10, 68
 Euler, H., and A., ammoniacal cyanacetate, condensation with its sodium derivative, 301
 Evans, W. H., electrolytic preparation of titanous sulphate, 313
 Exhibition, Historical Medical, St. Louis, awards, 209, 221, 245
 Exner, F. F., and E. F. Smith. (See Smith, E. F.)
 "Explosives, Report of His Majesty's Inspectors of" (review), 23
 Extensometers, calibration, interference apparatus for, 242
- FARADAY** Society, 231, 292
 Farmer, R. C., and F. J. Warth, affinity constants of aniline and its derivatives, 302
- "Fats, Oils, and Waxes, Chemical Technology and Analysis of" (review), 127
 Fawsitt, C. E., decomposition of methylcarbamide, 277
 Fenton, H. J. H., influence of radiations on atmospheric oxidation in presence of iron, 168
 mesoxalic semialdehyde, 155
 reaction for keto-hexoses, 182
 and J. P. Millington, colour reaction for methylfurfural and its derivatives, 182
 Ferchland, P., "Die Elektrochemische Industrie Deutschlands" (review), 116
 Fermentation, lactic acid, of, decomposing, 70
 Ferry, P., and G. Arth. (See Arth, G.)
 Finnmore, H., and J. Wade. (See Wade, J.)
 Fischer, E., and F. Schlotterbeck, conversion of sorbic acid into amino-acids, 46
 Flame spectra, 13
 Flood, deposits of the Hunter and Hawkesbury rivers, 280
 Flour and starch compositions, 195
 Flowers of Butea frondosa, colouring matter of, 32
 Fluorescence, 25, 203
 "Food Inspection and Analysis" (review), 326
 "Foods, Analysis of, and the Detection of their Adulteration" (review), 327
 Force, electromotive, transformation of thermo-chemical energy into, 41
 Formaldehyde, atmospheric, 70
 condensation with acetone, 265
 Forster, M. O., action of magnesium alkyl halides on derivatives of camphor, 278
 Fosse, R., action of trace of certain salts and caustic alkalis on diphenylcarbonic ether, and P. Bertrand, an organic persulphate, 256
 Francis, F. E., and O. C. M. Fide, action of nitrogen sulphide on organic substances, 277
 Frankland, P. F., and J. Harger, position isomerism and optical activity, 277
 and D. F. T. Wigg, Grignard reaction applied to esters of hydroxy-acids, 302
 French, H. T., rock sections, 161
 Freudenf. P., reduction of o-nitrobenzyl alcohol, 23
 Friend, J. A. N., influence of potassium persulphate on estimation of hydrogen peroxide, 275
 Friswell, R. J., improved form of Kipp's apparatus, 154
 Fucose and rhodose, antipodal isomerism, 304
 "Furnace, Electric" (review), 243
 Fusion-points, determination, 27
- GADOLINIUM**, yttric earth near to, 287
 Galadose, crystallization, 250
 Galvanometers, 267
 "Galvanoplastic" (review), 82
 Galway, Queen's College, 134
 Garrett, A. E., and R. S. Willows, chemical dissociation and electric conductivity, 21
 "Gas Manufacture, Chemistry of" (review), 327
 "Gas Works, their Construction and Arrangement" (review), 11
 Gas, sulphurous acid, and salts, compounds, 58
 Gases absorption by charcoal and coke, 109
 action on glass in neighbourhood of heated metals, 180
 ionisation, recording, 23
 newly discovered, probable presence in sun, 103
- Gases occluded in charcoal at low temperatures, absorption and thermal evolution, 73
 volatile, and acid separation without liquefaction, 90
 Gatecliff, J., and J. B. Cohen. (See Cohen, J. B.)
 Gaul, H., and E. Blaise. (See Blaise, E. E.)
 Geisel, E., and O. Ruff. (See Ruff, O.)
 Gelatin rendered insoluble by salts of sesquioxide of chromium, composition, 35
 treated with metallic chromates, action of light on, 35
 Gelstharp, F., electrolytic preparation of iron paste, 324
 Geometrical optics, curvature-method of teaching, 279
 "Germany, Electro-chemical Industry of" (review), 116
 Gernez, D., form taken by thallous iodide when going into solution, 117
 red and yellow varieties of thallous iodide, 56
 Gieseler, F., emanium, 259
 Ginzburg, A., applications of permanganates to determination of constitution of the amines and of other ammonium compounds, 269
 Girdle, and others, "Analyse des Matières Alimentaires et Recherche de Leurs Falsifications" (review), 327
 Glasgow and West of Scotland Technical College, 133
 Glass, action of gases on in neighbourhood of heated metals, 180
 Glucium, argon, and tellurium, atomic weights, irregularities of, 260
 atomic weight revision, 61, 75
 Glucoses, stereoisomeric, 32
 Glucose coloured blue by iodine, 132
 Glue, 19
 Glycerides, higher, 23, 235
 Glycol, pentamethylene, synthesis, 69
 bromoacetate, condensation with acetoacetic acid and acetone-carbonic ethers, 82
 Godchet, M., tetrahydride and octohydride of anthracene, 256
 Goguelia, G., and H. Cantoni. (See Cantoni, H.)
 "Gold Assaying" (review), 115
 Gold, action of hydrochloric acid on, 10
 determination, limit of error in, 240
 dissolution in aqueous potassium cyanide, influence of sunlight on, 275
 in dilute solution, isometric determination, 238
 in same group with the alkaline metals, attempt to explain, 271
 Goldsmith's Institute, 135
 Goldstein, E., withdrawal of oxygen by platinum, 117
 Gostger, M., and L. E. Cone, action of light on triphenylmethyl, 256
 Goodrich, W. F., "Small Destructors for Institutional and Trade Waste" (review), 243
 Gorgeu, A., series of artificial quadratic spins of the haussmannite type, 35
 Gourmand, M., and L. Bouvauet. (See Bouvauet, L.)
 Gravity and chemical action, 53
 Gray, T., and G. G. Henderson. (See Henderson, G. G.)
 Green, A. G., colouring matters of the fuchsine group, 253
 F. Sholefield, and E. Marden, colouring matters of the stilbene group, 254
 Green, Schwenfurt's, composition of, 117
 Greet, L., and G. Charpy. (See Charpy, G.)
 Grignard reaction applied to the esters of hydroxy-acids, 302

- Grossmann, H., and P. von der Forst, double cyanides of mercury, 317.
- Groth, P., crystal structure and its relation to chemical constitution, 142.
- Grune, H., phosphorescing zinc sulphide, 235.
- Guaiacol, distillation with lead oxide, 45.
- Guaiacum oxidation, influence of salts and organic substances on, 275.
- Guerin, G., derivatives of lauric acid, 35.
- hydroxy-lauric acid, 35.
- undecylmethylketone, 36.
- Guillet, L., constitution and properties of chromium steels, 160.
- of molybdenum steels, 232.
- of tungsten steels, 227.
- investigations on cementation of carbon steels, and other varieties of steels, 44.
- vanadium steels, 145.
- Guinchant and Chretien, MM., allotropic forms of antimony sulphide, 70.
- heat of formation of antimony trisulphides, 117.
- Gum, absence in kinds of *Eucalyptus*, 63.
- Gunning Victoria Jubilee Prize, 281.
- Guth, M., and A. Martens. (See Martens, A.)
- Guthrie, F. B., and T. W. E. David, flood deposits of the Hunter and Hawkesbury river, 281.
- Guttman, L. F., "Percentage Tables for Elementary Analyses" (review), 255.
- Guyot, P. A., and M. St. Bogdan, atomic weight of nitrogen, 34.
- Guyot, A., and A. Haller. (See Haller, A.)
- H₂O₂ action on carbohydrates in presence of ferrous sulphate, 135.
- Haas, J., and R. Doht. (See Doht, R.)
- Hadfield R. A., productions of magnetic alloys from non-magnetic metals, 182.
- Hall, A. D., effect of long-continued use of sodium nitrate on constitution of the soil, 18.
- mechanical analysis of soils, 17.
- J. W., and F. W. Harbord. (See Harbord, F. W.)
- W. T., and P. P. Treadwell. (See Treadwell, F. P.)
- Haller, A., and A. Guyot, synthesis in anthracene series, 70.
- and F. March, condensation of glycolbromide with acetoacetic and acetonediacarboxylic ethers, 32.
- influence of the combination of non-saturated radicals with certain molecules on their reactivity power, 56.
- Hall, J. L., action of zinc on sodium tungstates, 117.
- Halogens and oxygen, 191.
- Hammett, J., synthesis in pentamethylene series, 45.
- J. L., synthesis of pentamethylene glycol, of nitrile, and pimeic acid, 67.
- Hann, A. C., O. Hano, and A. Hann, Lapworth, reactions involving addition of hydrogen cyanide to carbon compounds, 255.
- Hannay, J. B., note on higher glycides, 223, 235.
- Hannay, F. K., and R. S. Morrell. (See Morrell, R. S.)
- Hantzsch, A., "Grundriss der Stereochemie" (review), 268.
- Harbord, F. W., and J. W. Hall, "Metallurgy of Steel" (review), 133.
- Harger, J., and P. F. Frankland. (See Frankland, P. F.)
- Harmonic analysis, approximate, 315.
- Harries, C., decomposition of paracautchouc by means of ozone, 95.
- varieties of caoutchouc, 304.
- Hart, E. B., and A. J. Patten. (See Patten, A. J.)
- Hartley, W. N., absorption spectrum of β -nitrosodimethylamine, 20.
- spectrum, generally attributed to chlorophyll, 21.
- Hartog, W. G., "Lectures Scientifiques" (review), 268.
- Hausmann, O., double hydrosulphites of the alkalis and bismuth, 71.
- Hawkesbury and Hunter rivers, flood deposits of, 280.
- Heikbrun, R., "Elementare Vorlesungen über Telegraphie und Telephonie" (review), 9.
- Helium, condensation by charcoal, 145.
- employment as a thermometric substance and its diffusion through silica, 304.
- Henderson, G. G., and T. Gray, action of chromyl chloride on stilbene, styrene, and phenanthrene, 250.
- Hendrickson, W. S., method for determination of chloric acid, 325.
- Henriet, H., atmospheric formaldehyde, 70.
- Hermann, J., and W. Traube. (See Traube, W.)
- Herreschmidt, H., extraction of vanadium from naturally occurring lead vanadate, 269.
- precipitation of sodium vanadate liquors, 316.
- Hexahydroacetophenone, 11.
- Hibbert, H., S. H. Beard, and J. J. Sudborough. (See Sudborough, J. J.)
- and J. J. Sudborough. (See Sudborough, J. J.)
- Historical Medical Exhibition, 244.
- Hittorf, W., part played by diaphragms in electrolysis of saline solutions, 329.
- Hodgkinson, W. R., and A. H. Coote, reactions between ammonium salts and metals, 142.
- and Major A. E. Edwards. (See Edwards, Major A. E.)
- Hoffmann, K., and H. Moissan. (See Moissan, H.)
- Hofmann, K., characterisation of lead, 3.
- and W. Duca, phosphorescing substances, 208.
- Hofmeister, F., "Beitrag zur Chemie der Physiologie und Pathologie" (review), 35.
- Holland, A., and L. Bertiaux, electrolytic separation of nickel and zinc, 45.
- estimation of bismuth by electrolysis, 118.
- use of complex salts in electrolytic analysis, 215.
- Holt, A. jun., and C. H. Burgess. (See Burgess, C. H.)
- Howden, S., and F. Ibbotson. (See Ibbotson, F.)
- Hughes, S., and H. O'Connor, "Gas Works, their Construction and Arrangement" (review), 137.
- Hughes Medal, 250, 303.
- Hugot, C., action of ammonia gas on arsenic trichloride, tri-bromide, and tri-iodide, 70.
- Hundeshagen, L., occurrence of platinum in wolastonite, 77.
- Hunter and Hawkesbury rivers, flood deposits of, 280.
- Hydrothermal constitution, 2.
- Hydroxy-acids, 157.
- complete, 242.
- analysis, 247.
- Hydro-aromatic substances, 168.
- Hydrocarbides, di-halogen aromatic, organo-magnesium derivatives in the radicle, 57.
- Hydrocarbons, aromatic, synthesis, 328.
- of benzene series, electrolytic oxidation, 232.
- Hydrogen, absorption by rhodium, 271.
- and chlorine, union, 265.
- condensation by charcoal, 145.
- cyanide, addition to benzylideneacetophenone, 253.
- addition to carbon compounds, reactions involving, 251, 253.
- addition to unsaturated compounds, 302.
- oxygen cell, potential of, 293.
- Hydroxide, and G. Persulphuric acid mixtures, effect of chloric acid on, 262.
- influence of potassium persulphate on, 275.
- of crystallization, 59.
- phosphide, arsenide, and antimonide, characteristic reaction of, 197.
- Hygrometer, sensitive, 242.
- Hydroxylic chromic behaviour towards oxalic acid and certain other organic acids, 254.
- Hydroxy acids, esters of, Grignard reaction applied to, 302.
- Hydrous amorphous silica, 117.
- Hysteresis, magnetic, variations with frequency, 266.
- IBBOTSON, F., and R. Howden, determination of chromium in steel, 320.
- Imino-compounds, formation and reactions, 301.
- "Imperide, chromat, Technical Reports and Scientific Papers" (review), 254.
- Imperial College of Chemistry and Pharmacy, 136.
- Indazolic derivatives, formation, 19.
- Indole, chemistry of, 19.
- Java, constituent, 33.
- Indium, 45.
- Indrisson, T., experiments with indium, from bromide of indium, 45.
- Ingle, H., available plant food in soils, 265.
- Inglis, J. K., and R. Luther. (See Luther, R.)
- Institute of Chemistry, 47, 58, 136, 281.
- Iodide, aurous, preparation by action of iodine on gold, 274.
- thallous, form taken when going into solution, 117.
- red and yellow varieties, 55.
- Iodine, action on acids of ethylene series, 325.
- atomic weight, 49.
- compounds, obtained with metanitriline, 35, 70.
- pure, preparation, 27.
- Iodograph, 23.
- Iron and separation, 215.
- determination of total sulphur in by evolution, 326.
- in ferric state, iodometric estimation, 64.
- malachite, 23.
- malachite, in persulphate method of estimating, 237.
- Irons, determination of sulphur in, 237.
- Irving, J. C., and A. Cameron, solution in ligalactose, 234.
- and I. P. de la. See Purdie, F.
- JACKSON, H. C., "Directions in Laboratory Work in Physiological Chemistry" (review), 9.
- Jahn, S., and A. Coehn. (See Coehn, A.)
- Janasch, P., and W. Bettes, determination of paracautchouc by means of ozone, 95.
- Janasch, P., and W. Bettes, separation of mercury from molybdenum and tungsten by means of hydrazine, 46.
- Japp, F. R., and W. Matland, α -benzoyl- β -trimethylacetyl-styrene, 277.
- interaction of sodium phenylglycidate with phenylhydrazine, 277.
- reduction products of α -dimethylamylacetonebenzyl, and condensation products of benzaldehydes with ketones, 277.
- and J. Wood, preliminary notice of some condensations of phenanthraquinone with ketones, 391.
- Jaquero, A., and F. L. Perrot, employment of helium as a thermometric substance, and its diffusion through silica, 304.
- and A. Pintza, densities of sulphurous anhydride and oxygen, 82.
- and M. St. Bogdan, determination of atomic weight of nitrogen, 70.
- Jakes, A., natural chemical rule, 107.
- Jaubert, G. F., action of boric acid upon alkaline peroxides and formation of perborates, 304.
- Java indigo, constituent, 33.
- Joannis, A., action of ammonia on boron bromide and phosphorus chloride, 118.
- cuprous salts, 34.
- Jones, D. T., and G. Tattersall, new synthesis of iso-caprolactone and derivatives, 290.
- H. O., constitution of nickel carbonyl, 144.
- stereochemistry of nitrogen, 193.
- Jorgensen, S. M., pure rhodium, 72.
- Jorissen, W. P., and W. E. Ringer, phosphorescing zinc sulphide, 305.
- Jungfleisch, E., method of decomposing lactic acid of fermentation into its components active to polarised light, 70.
- KÄHLBERG, L., recent investigations bearing on theory of electrolytic dissociation, 292.
- Kauffman, H., fluorescence, 208.
- radon rays and benzene derivatives, 216.
- and A. Weisswenger, fluorescence, 95.
- "Kelly's Directory of Chemists and Druggists" (review), 24.
- Keto-hexones, reaction for, 182.
- Ketones, acetylenic, 252.
- aromatic, action of reduced nickel on, 328.
- condensation products of benzaldehydes with, 277.
- unsaturated, and metallic chlorides, compounds, 257.
- King, C. H., 125, 297.
- Knappe, 151, 296.
- Kling, A., action of ammoniacal nitrogen on metallic cyanides, 3.
- oxidation of acetal, 293.
- Knecht, P., action of hydrogen on water, 23.
- Knecht, P., action of hard water, 9.
- S. S., determination of total sulphur in iron by evolution, 326.
- Kubischwiler, V., action of nitric acid on metallic salts, 24.
- and M. Knecht, metallic salts, 24.
- Kohn, A., action of ammoniacal powder and oxidation of aluminium, 5.
- atomic weight of a uranium, 250.

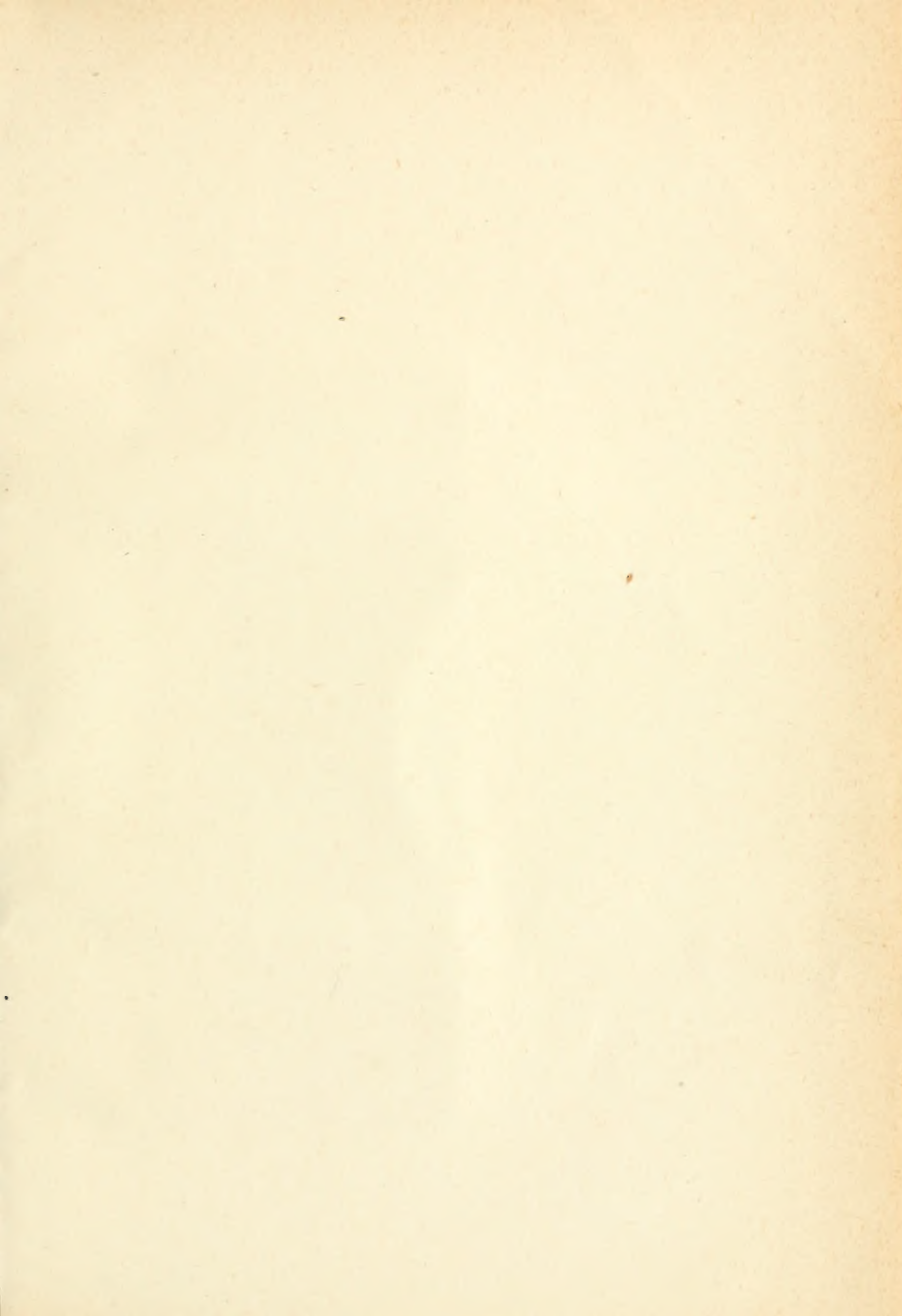
- Kothner, P., and E. Aeuer, atomic weight of iodine, 94
- Kraft, F., boiling and evaporation of metals in a cathodic vacuum, 47
- Kuhling, O., use of tetroxalate of potassium in titration, 91
- Kunst analysis, 83
- Kutscheroff, M., and V. Kohl-schutter. (See Kohlschutter, V.)
- L**ABELS, reagent, 249
- Labile stereoisomerides, influence of radium radiations on, 31
- "Laboratory. Chemical, Elementary Manual for (review), 267
- Laby, T. H., and D. Mawson. (See Mawson, D.)
- Lacombe, H., and G. Urbain. (See Urbain, G.)
- Laloue, G., and E. Charabot. (See Charabot, E.)
- Lambrecht, R., and H. Weil, rapid method of distinguishing rosaniline and pararosaniline, 208
- Lantern incandescent and arc, determination of mean spherical candle-power of, 266
- Lander, G. D., and H. E. Laws, amidechlorohydrate, 290
- Lange, J. H., and R. Meldola. (See Meldola, R.)
- Lantern for science lectures, 267
- Lanthanum and thorium, separation by metanitrato-benzoic acid, 196, 201
- Lapworth, A., note on addition of hydrogen cyanide to unsaturated compounds, 302
- reactions involving addition of hydrogen cyanide to carbon compounds, 251
- and A. C. O. Hann. (See Hann, A. C. O.)
- Lauth, C., oxidation of orthonitrotoluene, 141
- Lavoisier gold medal, 305
- Law, H. D., and F. M. Perkins. (See Perkins, F. M.)
- Laws, H. E., and G. D. Lander. (See Lander, G. D.)
- Lazard, L., and W. Ostwald. (See Ostwald, W.)
- Le Sueur, H. R., oleic acid, 278
- Leach, A. E., Food Inspection and Analysis" (review), 326
- Leach, F. P., and W. A. Tilden. (See Tilden, W. A.)
- Lead, characterisation of, 3
- in carbon group, attempt to explain occurrence of, 271
- radio-active, 92
- acetate and lead sulphate, crystalline compound of, 160
- Lebeau, P., decomposition of a mixture of calcium carbonate and an alkaline carbonate under action of heat in a vacuum, 34
- formation of isomorphous mixtures of lime and lithia, 44
- "Lescentes Scientifiques" (review), 268
- Leeds Institute Technical School, 126
- University of, 127
- Lehmit, R. A., "Electro-chemistry" (review), 159
- Lehmann, Dr. O., "Flüssige Kristalle" (review), 117
- Lemaître, H., estimation of perchlorate of sodium in commercial nitrate of sodium, 41
- Lemoult, P., certain derivatives of pentabasic phosphoric acid, 145
- characteristic reaction of hydrogen phosphide, arsenide, and antimonide, 197
- crystalline compound of lead acetate and lead sulphate, 160
- of combustion of sulpho-organic compounds, 82
- remarks upon a recent series of calorimetric determinations, 269
- Lenher, V., and H. Moissan. (See Moissan, H.)
- Lenses, apparatus for determining curvature, 279
- property of, 243
- Leroux, H., tetrahydride and decahydride of naphthalene, 293
- Lespicau, M., β -bromobutyric acid, 293
- Leucanilines and rosanilines, thermo-chemical comparison between, 223
- Levy, W., and A. Rosenheim. (See Rosenheim, A.)
- Lewis, W. H., and F. D. Chattaway. (See Chattaway, F. D.)
- Lewkowitch, Dr. T., "Chemical Technology and Analysis of Oils, Fats, and Waxes" (review), 197
- Ley, H., and K. Schaefer, research on dissociation of salts of the heavy metals, 57
- Light, action on triphenylmethyl, 256
- chemical effects of, 10
- lime, and lithia, isomorphous mixtures of, formation, 44
- determination, 248
- Limoneo, N., nitrosocyanides, 21
- Lindenbary, H., and L. Wolff. (See Wolff, L.)
- Lindet, L., influence of certain substances in promoting or retarding production of rust, 328
- Linseed oil, 194
- Liquids, stationary, measurement of potential of electrode in, 231
- Litha and lime, isomorphous mixtures of, formation, 44
- Lithography, 160
- Livinge, G. D., probable presence in sun of newly discovered gases, 103
- Liverpool University of, 128
- Liversidge, A., "Tables for Qualitative Chemical Analysis" (review), 254
- "Livingstone College Year-book" (review), 244
- Lockyer, Sir Norman, relation between spectra of sun spots and stars, 89
- "London. Essence Company Reports" (review), 254
- London, City and Guilds of, Institute, 71, 134
- City of, College, 135
- East, Technical College, 135
- University, 121
- water supply, 43, 106, 172, 201, 262, 314
- Losanitsch, S. M., radio-active cinnabarites, 217
- Lumière, A., and A. Seyewitz, composition of gelatin rendered insoluble by salts of sesquioxide of chromium, 35
- Luminescence of Sidot's blend under influence of ozone, 231
- Lunge, G., "Chemische-technische Untersuchungsmethoden" (review), 116
- Lutes, 184, 194
- Luther, R., and J. K. H. Inglis, chlorine considered as an oxidising agent, 119
- Lyle, T. R., investigation of variations of magnetic hysteresis with frequency, 266
- M**CCOY, H. N., origin of radium, 187, 199
- McIntosh, J. G., mechanical analysis of soil, 83
- Williamson's theory of etherification, 44
- McKenzie, A., studies in asymmetric synthesis, 251
- Magnesia cupels, 21
- estimation, ponderable or gasometric, 161
- Magnesium and aluminium alloys, 35, 45
- Magnesium and zinc alloys, 160
- alkyl compounds, action on halogen derivatives of phosphorus, arsenic, and antimony, 255
- halides, action on derivatives of camphor, 278
- halide of menthyl benzoyl-formide, 251
- bromide, anhydrous, additive compounds with organic oxygen and nitrogen compounds, 21
- α -naphthyl bromide, action of phthalic anhydride on, 276
- peroxide, 257
- phenylbromide, action of carbonic acid on, 276
- Magnetic hysteresis, variations with frequency, 266
- Maihe, A., and P. Sabatier. (See Sabatier, P.)
- Maitland, W., and F. R. Japp. (See Japp, F. R.)
- Makowska, O., and H. Erdmann. (See Erdmann, H.)
- Mahitano, G. E., colloidal state of matter, 329
- Manchester, Municipal School of Technology, 136
- Victoria University of, 129
- Mandarin orange tree, production and distribution of organic substances in, 244
- Mandel, J. A., and C. Arnold. (See Arnold, C.)
- Manganese in iron and steel, estimating, persulphate method, 237
- Maquenne, L., determination of fusion points, 27
- and L. Philippe, constitution of ricinine, 238
- March, F., and A. Haller. (See Haller, A.)
- Marçilly, L., oxypivalic acid, 148
- and E. E. Blaise. (See Blaise, E. E.)
- Marie, C., boiling-point constants of mixtures, 255
- certain mixed phosphorus derivatives of hypophosphorous acid, 57
- Marsden, F. A., G. Green, and F. Scholefield. (See Green, A. G.)
- Marshall, H., abstracting of current chemical literature, 283
- Martens, A., and M. Guth, "Das Königliche Materialprüfungsamt der Technischen Hochschule, Berlin" (review), 146
- Martin, G., changes induced in properties of elements by them under other external conditions than those common in the laboratory, 189
- method of representing the properties of elements graphically by means of characteristic surfaces, 175
- Massel, L., and E. Boulanger. (See Boulanger, E.)
- Matter, colloid of, 329
- reactions suggested by new theory of, 85
- Mawson, D., and T. H. Laby, radio-activity and occurrence of radium in Australian minerals, 280
- Maxson, R. N., iodometric determination of gold in dilute solution, 238
- limit of error in volumetric determination of small amounts of gold, 240
- Mayer, C., condensation by means of acids of phenols and aromatic amines with aniline benzylidenes, 45
- Mayer, H., "Die Neuren Strahlungen" (review), 146
- Measurement of small differences of phase, 278
- Melander, C., Chemical Synthesis of Vital Products and the Inter-relations between Organic Compounds" (review), 221
- Meldola, R., and J. H. Lane, isomerism of the amides of the naphthalene series, 283
- Mellor, J. W., union of hydrogen and chlorine, rate of decay of activity of gaseous chlorine, 265
- Melting-points, determination, 284
- Mendeleeff, D., "Chemical Connection of the Ether" (review), 326
- Menthyl benzoylformate, action of magnesium alkyl haloids on, 251
- reduction, 251
- Mercurising, effect on dye affinity, 179
- Mercury and molybdenum, separation, 46
- and tungsten, separation, 46
- nitro-salts, 59
- occurrence in same group with alkaline earths, 271
- cyanides, double, 317
- nitrate, conversion of mercurous nitrate into, 289
- oxides, red and yellow, solubility and dissociation, 47
- oxide, yellow, action on acids of ethylene series, 328
- Mesityl oxide, action of potassium cyanide on, 251
- Metalloids, tri- and penta-valent, action of halogen derivatives of, upon alkyl halogen compounds, 269
- "Metallurgy of Steel" (review), 33
- Metals and ammonium salts, reactions between, 142
- boiling and evaporation in vacuum, 47
- distillation of a mixture of two, 56
- evolution of structure in, 160
- heated, action of gases on glass in a neighborhood of, 180
- heavy, dissociation of salts of, 59
- industrial separation by double decomposition, 316
- non-magnetic, production of magnetic alloys from, 180
- polyatomic, chromates of, 95
- Metanitraulines, iodine compounds obtained with, 35, 70
- Meqorite, Canon Diablo, 295
- Methyl arsenic, 179
- carbamide, decomposition, 277
- furfural, and derivatives, colour reaction for, 182
- Mettler, C., electrolytic reduction of aromatic esters, 257
- Meyer, F., preparation of aurous iodide by the action of iodine on gold, 274
- O., chromates of the polyatomic metals, 95
- R., constitution of phthalic salts, 166
- Micklethwait, Frances Mary Gore, and J. Morgan. (See Morgan, G. T.)
- Microbes, nitrifying, 329
- examination, 11
- Mihl, F., and K. Schenck. (See Schenck, K.)
- Milner, E. H., "Quantitative Analysis for Mining Engineers" (review), 9
- and F. van D. Cruser. (See Cruser, F. van D.)
- J., and I. B. Cohen. (See Cohen, J. B.)
- Millington, J. P., and H. J. H. Fenton. (See Fenton, H. J. H.)
- Minerals, characteristic sulphur lines in photographic spectroscopy of, 140
- Mohr, E., proof of racemic character, 95
- Moissan, H., researches upon the Canon Diablo meteorite, 295
- and K. Hoffmann, new carbide of molybdenum, 44, 208
- and V. Lenher, "Electric Furnace" (review), 243

- Moissan, H., and M. O'Farrell, dissociation of a mixture of two metals, 56
and F. Siemens, action of silicon on water below 100°, 58
solubility of silicon in silver, 94
Möller, J., "Die Elektrochemische Untersuchung des Nitrates der Organischen Verbindungen" (review), 149
Molybdenum and mercury separation, 46
narrow and flat steel-making alloys, determination, 204, 210
carbide, 44, 208
steels, properties and constitution, 232
Monophenylurea, action of nitrous acid on, 234
Morgan, G. T., notes on analytical chemistry, 1
and Frances Mary Gore Micklethwait, 6-aminocoumarin, 251
Murrell, R. S., and A. E. Bellars, action of H_2O_2 on carbohydrates in the presence of ferrous sulphate, 153
and K. H. Hansson, isomerism of *a*- and β -ketonic acids, 166, 264
Morrow, J., and E. L. Watkin, interferometer apparatus for the calibration of extensometers, 242
Moss, S., artificial silk, 83
Mourou, C., chemical composition of radio-active gaseous mixtures arising from hot springs, 328
and M. Brachin, β -silylacyl and β -oxyphenyl ethylenic acetones, 117
and R. Deange, acetylenic aldehydes, 10
Mueller, W., maximum density of aqueous solutions of some organic bodies, 11
Muir, M. M. F., "Elements of Chemistry" (review), 33
Müller, W. J., and F. Suckert, products of decomposition of brom-succinic acid and its salts in aqueous solution, 94
Muliken, S. P., "Method for the Identification of Pure Organic Compounds" (review), 69
N-RAYS in chemistry, 11
Namas, R., and L. Carcano, iodometric estimation of iron in the ferric state, 64
Naphthacenequinone, halogen derivatives, 250
Naphthalene, halides of, 251
Naphthalene series, aminides of isomerism, 283
tetrahydride and decahydride of, 281
Narcosis, 152
Nesbitt, A. C., new separation of thorium from cerium, lanthanum, and didymium, by metanitrobenzoic acid, 196, 201
New South Wales, Royal Society of, 68
Newcastle-on-Tyne, Durham College of Science, 129
Newton, J. A., and T. S. Price, 132
Nickel analysis, electrolytic, 307
and zinc separation, 215
electrolytic, 45
detection, 169
reduced, action on aromatic ketones, 328
carbonyl constitution, 144
Nitrate, thallous, 56
Nitrite, synthesis, 69
Nitrite, mercurous, production, and conversion into mercury nitrates, 289
Nitrates, determination in absence of air, 114
Nitrates of alkali metals, and metals of alkaline earths, and decomposition by heat, 301
Nitrogen and oxygen compounds, additive compounds of, 21
hydrous magnesium bromide with, 21
atom, pentavalent, 192
atomic weight of, 34, 269
determination, 70
compounds, quivalent, 193
trivalent, 193
nitric, estimating by Pelouze-Fresenius method, 57
stereochemistry of, 193
chloro-iodides containing two halogen atoms attached to the nitrogen, 31
iodide constitution, 264
derivatives, metallic, 301
monoxide, density, 269
protoxide, analysis by weight, 34
sulphide, action on organic substances, 277
Nitro-compounds, of Organic Compounds, Electrochemical Reduction of the" (review), 146
Nitroso-compounds, metallic, 208
Nitrosodimethylamine, *p*, absorption spectrum of, 20
Nobel prizes, 309
Nordmann, C., method of continuous recording of ionisation of gases, 197
Nottingham, University College, 130
Noyes, A. A., and D. A. Kohn, equilibrium of solution between chloride and silver. Side of silver, and solutions of potassium chloride and potash, 59
W. A., present problems of organic chemistry, 214, 225
OBITUARY. Sir Isaac Lowthian Bell, 316
O'Connor, H., and S. Hughes (See Hughes, S.)
O'Farrell, M., and H. Moissan (See Moissan, H.)
Oil, bergamot, 252
olive, refractive index of, 146
insoluble, 194
"Oils, Fats, and Waxes, Chemical Technology and Analysis of" (review), 157
Oils, origin of, 256
of citrus series, 252
Olefinic ketonic compounds, 278
action of organic bases on, 182, 250
Olson, J. C., "Text-book of Quantitative Chemical Analysis" (review), 268
Opalescence phenomena, observed in the neighbourhood of critical states, 139
Optical activity, and position isomerism, 251, 277
Optically active compounds, influence of solvents on rotation of, 20
Orange tree, mandarin, production and distribution of organic substances in, 244
"Organic Compounds, Method for the Identification of Pure" (review), 69
Organic bases, action on olefinic ketonic compounds, 182, 250
bodies, maximum density of aqueous solutions of, 11
compounds, analysis, 250
substances, analysis, use of sodium peroxide for, 46
in mandarin orange tree, production and distribution, 244
Organic-halogen-magnesium derivatives, action of oxygen on, 11
Organic-magnesium bromides, effect of anhydrides on, 276
compounds, action on phenylamide and phenylphthalimide, 70
Organic-magnesium derivatives, aromatic, action of chlorides of phosphorus on, 281
Orndorff, W. K., and S. Salkowski (See Salkowski, S.)
Orthonitrotoluene, oxidation, 148
Osmond, F., and G. Gartaud, scientific phenomena accompanying polishing, 147
Osmotic, 137
Otsu, J. W., and M. Hottenstein, "Gesammelte Abhandlungen von Robert Bunsen" (review), 149
and L. Izard, "Revue de Chimie Inorganique" (review), 267
Owens College, Victoria University of Manchester, 129
Oxalates, decomposition by heat, 18
Oxford University, 121
Oxidation, atmospheric, influence of radium radiations on, in presence of iron, 168
Oxide, determining presence in qualitative analysis, 33
nitric, action on chromous salts, 233
nitrous, density, 153
Oxycarbonate and silicate cements, 194
Oxygen, action on organo-halogen-magnesium derivatives, 149
acids, in organic persulphates, determination, 233
and halogens, 191
and nitrogen compounds, additive compounds of anhydrous magnesium bromide with, 21
and sulphur, 191
basic properties, 265
density, 82
withdrawal by platinum, 317
Ozone, considered as an oxidising agent, 119
luminescence of Sidoti's blends under influence of, 233
PAUL, C., and F. Voss, colloidal silver salts, 304
Page, T. H., and H. E. Burgess (See Burgess, H. E.)
Palladium determination, 89
and separation from other metals, 46
Paracoucou, decomposition by means of ozone, 96
Parasaccharine and rosaniline, distinguishing, 208
Parrot, F. L., and A. Jaquero, (See Jaquero, A.)
Parsons, C. L., revision of the atomic weight of beryllium, 61, 73
Paete, tin, preparation, electrolytic, 324
Patent Law, 1904, 147
"Pathology and Physiology, Chemical Contributions to" (review), 34, 51
Patten, A. J., and E. B. Hart, 115
nature of the principal phosphorus compound in wheat bran, 112
Patterson, T. S., influence of solvents on rotation of optically active compounds, 20
Paul, R. W., exhibition of apparatus, 277
Pechoux, H., alloys of aluminium with bismuth and magnesium, 35
with magnesium and antimony, 45
Pentamethylene series, synthesis in, 45
Pentabenzol, di-amylene of, 45
Pentabenzol, di-amylene of, 34
Pentabenzol, new theory of, 159
Perkin, A., colouring matter of the flowers of Butea frondosa, 32
constituent of Java indigo, 33
cyanomacrium, 32
determination of acetyl group, 32
Perkin, A. G., note on the cathodes, 132
P. M., and F. D. Law, electro-lytic oxidation of hydrocarbons of the benzene series, 232
and W. C. Prebble, electrolytic analysis of cobalt and nickel, 305
W. H., jun., Davy medal, 259, 343
Perrin, R. P., decomposition and synthesis of ammonia, 182
and G. A. S. Atkinson, decomposition of ammonia by heat, 13
Permanganates, application to the determination of the constitution of the amines and of other ammonium compounds, 269
Peroxis, nitric, constitution, 65
Perron, R. L., and A. Jaquero, (See Jaquero, A.)
Persulphate, organic, 256
Persulphates, organic, determination of active oxygen in, 233
Petit, J., and A. Brochet, (See Brochet, A.)
Pflanzhaus, "Galvanoplastik" (review), 82
Pharmaceutical Society of Great Britain, School of, 124
Phase measurement of small differences, 278
Pheps, I. K., determination of nitrates in absence of air, 114
use of tereous sulphate in estimation of chlorates and bromates, 195
Phenanthraquinone, condensations with ketonic compounds, 291
Phenanthrene, action of chromyl chloride on, 259
Phenols, condensation with aniline benzylidene, 45
Phenyladenine, 2, 46
Phenyldiazomethanobenzene, substitution derivatives, 263
Phenylene diamine, oxidation products of, 118
Phenylhydrazine, interaction of sodium phenylglycidate with, 27
Phenyl-hydroxanthine, 2, 4, 45
Phenyl isocyanate, action on univalent alcohols, 58, 70
Phenylphthalimide, action of mixed organo-magnesium compounds on, 70
Philippe, L., and L. Maquenne, (See Maquenne, L.)
Phillips, H. J., "Gold Assaying" (review), 115
Phosphate, ferric, basic, 34
Phosphorescing substances, 208
Phosphorus, 227
action of magnesium alkyl compounds upon the halogen derivatives of, 26
compound in wheat bran, 112
derivatives, organic, preparing, 269
chloride, action of ammonia on, 115
chloride, action on aromatic organo-magnesium derivatives, 251
Photo-engraving, 160
Photographic plate, action of water on in dark, 104
"Photography, British Journal of" (review), 2
Phthalate salts, constitution, 166
Phthalic acid, action of mixed organo-magnesium compounds on, 70
"Physical Apparatus, Catalogue of" (review), 245
"Physical Chemistry, Elementary Treatise on" (review), 327
Physical Society, 212, 246, 266, 278, 315
Physics and chemistry, handbook of, 24
Nobel prize for, 309
"Physiology and Pathology, Chemical Contributions to" (review), 34, 51

- Pickles, S. S., and C. Weizmann, effect of anhydrides on organo-magnesium bromides, 276
halogen derivatives of naphth-acenequinone, 290
Pichet, A., and H. C. Biddle, "Vegetable Alkaloids" (review), 44
Pintza, A., and A. Jaquerod. (See Jaquerod, A.)
Pissarski, L., state in which some superoxygenated acids and their salts exist in solution, 11
Pitch, 183
Plant food in soils, available, 265
Plaster of Paris, 184
Plastic materials, 209
Platinum, action of hydrochloric acid on, 10
ammoniacal compounds, 83
colloidal, effect on mixtures of Caro's persulphuric acid with hydrogen peroxide, 262
electrolytic solution, 310
in wollastonite, 77
with withdrawal of oxygen by, 317
Plotnikov, V. A., electric conductivity of solutions in bromine, 269
Poisoning by ptomaine, 23
Polonium, 92
Poising, scientific phenomena accompanying, 117
Pollok, J. H., composition of beryl, 263
Polytechnic, 136
Pool, Miss Buena, note on a suggested new source of aluminium, 232
Pope, W. J., and G. Clark, jun., resolution of externally compensated dihydro- α -methyl-indole, 233
Position, isomerism and optical activity, 251, 277
Potassium chloride and potash solutions, chloride of silver and oxide of silver, equilibrium of solution between, cyanide, action of cyanogen on, 56
action on mesityl oxide, 251
ferrocyanide oxidation, electrolytic, influence of nature of anode upon, 328
oleate solution, use for determination of hardness of waters, 55
persulphate, influence on estimation of hydrogen peroxide, 275
tetroxalate, use in titration, 91
Potential of electrode in stationary liquids, measurement, 231
of the hydrogen-oxygen cell, 293
Poulenc, C., "Les Nouveaux Chimiques pour 1904" (review), 22
Pozz-Escot, E., azoic dyes derived from 2,2-dinaphthyl, 45
examination and synthetic preparation of certain symmetric cyclic thiourides, 173
"Traité Élémentaire de Physico-Chimie" (review), 327
Prebble, W. C., and F. M. Perkin. (See Perkin, F. M.)
Prentice, B., constitution of pyrazolone derivatives, 290
Price, T. S., and J. A. Newton, effect of colloidal platinum on mixtures of Caro's persulphuric acid with hydrogen peroxide, 262
Fringsheim, H. H., use of sodium peroxide for the qualitative analysis of organic substances, 46
Prussian blue estimation, 78
Peschor, K., and M. Silberbach, distillation of guaiacol with lead oxide, 45
Ptomaine poisoning, 23
Pulsifer, H. B., radically new method for the determination of sulphur in iron and steels, 230
Purdie, T., and J. C. Irvine, stereoisomeric tetramethyl methylglucosides and tetramethyl glucoside, 250
Pyrene series, researches in the, 82
Pyrazolidone derivatives, constitution, 290
Pyridine bases, action on bromo-succinic and dibromo-succinic ethers, 328
Pyrocatechin homologues, 57
Pyrene compounds, constitution, 19
QUENNESSEN, L., absorption of hydrogen by rhodium, 271
Quinoline bases, action on bromo-succinic and dibromo-succinic ethers, 328
RABISCHONG, J., action of chloride of diazobenzene on substituted oxyalkyl ethers, 71
of diazoic chlorides in excess in alkaline solution on oxalacetic ether, 70
on the oxalacetic ethers, 70
Racemic character, proof of, 95
Radicles, non-saturated, and molecules, influence of combination on rotatory power, 56
Radio-active cinnabar, 217
gaseous mixtures arising from hot springs, chemical composition, 328
"Radio-activity and Electronics, Journal of" (review), 34
Radio-activity, 2
experiments in, 149
Radio-tellurium, 92
Radium, 25
compounds, bearing of the colour phenomena presented by, 157
emanations, action on diamond, in Australian minerals, 280
origin of, 187, 199
radiations, influence on atmospheric oxidation in presence of, 168
on labile stereoisomerides, 31
rays and benzene derivatives, 216
bromide emanation experiments, 95
Ramsay, Sir W., Nobel prize for chemistry, 300
Raper, H. S., and J. B. Cohen. (See Cohen, J. B.)
Ray, P. C., nitrates of the alkali metals and metals of the alkaline earths and their decomposition by heat, 301
theory of the production of mercuric nitrate and of its conversion into various mercury nitrates, 259
Rayleigh, Lord, density of nitrous oxide, 153
Nobel prize for physics, 300
"Kays, Newer" (review), 140
Reaction for keto-hexoses, 182
Grignard, applied to the esters of hydroxy-acids, 302
of hydrogen phosphite, arsenide, and antimonide, 197
Reactions, chemical, possibility of, 328
involving the addition of hydrocyanide to carbon compounds, 251, 253
Reagent labels, 249
Reduth School of Mines, 136
Refractive indices of the elements, 133
Remifry, F. G. P., H. Baron, and J. F. Thorpe. (See Baron, H.)
Renou, Nora, and A. W. Crossley. (See Crossley, A. W.)
Renz, C., indium, 45
"Report, Annual, on Alkali, &c., Works" (review), 147
"Report, London Essence Company" (review), 245
"Report of His Majesty's Inspectors of Explosives" (review), 22
Report of committee appointed to consider the standardisation of methods for the bacterioscopic examination of water, 177
on cadmium cell, 225
Resin, 194
Rhodose and fucose, antipodal isomerism, 304
Rhodol synthesis, 57
Rhodium, absorption of hydrogen by, 271
pure, 271
Richards, P. A. E., "Practical Chemistry" (review), 146
Ricinine constitution, 328
Riegler, E., ponderable or gasometric estimation of phosphoric acid and magnesia, 161
Riggs, W., "Elementary Manual for the Chemical Laboratory" (review), 267
Ringer, W. E., and W. P. Jorissen. (See Jorissen, W. P.)
Robertson, W., studies on comparative cry-scropy, 291
Rock sections, 161
Rosaniline, ammoniacal additive compounds, 57
and rosaniline, distinguishing, 258
polyacids, 35
salts, constitution, 256
hydrochloric additive compounds of, 45
Rosaniline and leucanilines, thermo-chemical comparison between, 232
nomenclature, 207
tetraoxycyclohexane, 207, 281
Rosenheim, A., and L. Singer, preparation of alkyl sulphonic acids, 45
and W. Levy, compounds of unsaturated ketones with metallic chlorides, 257
Royal College of Science and Royal School of Mines, 123
Dublin Society, 33
Institution, 30, 244, 245, 293, 294, 314
Medal, 250
Society, 250, 302
of New South Wales, 65, 280
Rubber, 194
Ruff, O., preparation of sulphamide, 161
and E. Geisel, so-called magnesium peroxide, 257
Ruhemann, S., olefinic ketonic compounds, 278
and E. Watson, action of organic bases on olefinic ketonic compounds, 182, 250
Rumford, 250, 303
Rumford, M., estimation of tannin with ferric salts, 249
Rust production, influence of certain substances in promoting or retarding, 328
Rusell, W. J., action of wood on a photographic plate in the dark, 104
Rutherford, E., Rumford Medal, 250, 303
SABATIER, P., and A. Maithe, synthesis of a series of tertiary alcohols derived from cyclohexanol, 10
synthesis of certain alcohols in the cyclohexane series, 118
Sadtler, S. S., lutes, 184, 194
St. Andrews, University of, 131
St. Bogdan, M., and P. A. Guye. (See Guye, P. A.)
and A. Jaquerod. (See Jaquerod, A.)
St. Louis Exhibition awards, 209, 221, 245
Saline solutions, electrolysis, part played by diaphragms in, 329
Salkowski, E., and W. R. Orndorff, "Laboratory Manual of Physiological and Pathological Chemistry" (review), 9
Salts, action on diphenylcarbonic ether, 83
ammonium, and metals, reactions between, 142
and acids, superoxygenated in solution, 11
and sulphurous acid gas, compounds, 58
chromous, action of nitric oxide on, 235
complex, use in electrolytic analysis, 215
cuprous, 34
of carbinol and cyclohexanetriamines, 221
of heavy metals, dissociation, 59
of metals and ammonia compounds, 107
of rosaniline, constitution, 256
hydrochloric, additive compounds of, 45
phthaline, constitution, 166
Sand, H. J. S., measurement of the potential of the electrode in stationary liquids, 231
Sanitary Institute, 47
Santonaria thymifera, 190
Saponaria, 183
Sander, A., action of the chlorides of phosphorus upon aromatic organo-magnesium derivatives, 281
Schaefer, K., and H. Ley. (See Ley, H.)
Schenck, J., phosphorus, 227
and F. Mühr, luminescence of Sidot's blends under influence of ozone, 323
Schier, J., solubility of the red and yellow oxides of mercury and their dissociations, 47
Schlotterbeck, F., and E. Fischer. (See Fischer, E.)
Schnudlin, J., ammoniacal additive compounds of rosaniline, 57
carbinol salts and cyclohexanerosanilines, 221
constitution of the rosaniline salts, 256
effect of low temperature upon dyes, 293
heat of combustion of triphenylmethyl and of derivatives of triphenyl methane, 293
hydrochloric additive compounds or rosaniline salts, 45
nomenclature of the rosanilines, 207
rosaniline polyacids, 35
tetraoxycyclohexane rosanilines, 207, 281
theory of dyes, 328
thermo-chemical comparison between rosanilines and leucanilines, 232
Scholfield, F. A. G. Green, and F. Marsden. (See Green, A. G.)
Schubert, G., action of carbonic acid on phenylbromide of magnesium, 247
Schweinfurt's green, composition of homologue of, 117
Scott, A., decomposition of oxalates by heat, 18
some alkyl derivatives of sulphur, selenium, and tellurium, 18
Selenium, alkyl derivatives, 18
Semialdehyde, mesoxalic, 155
Sener, A., and P. C. Austin, halides of the acridines and naphtharidines, 251
Seubert, K., place of tellurium in the natural classification of the elements, 71
Seybold, W., and A. Werner. (See Werner, A.)
Seyewitz, A., and A. L. Lumiere. (See Lumiere, A. L.)
Sheffield, University College, 59, 131
Schliac, 194

- Side-chain, influence of substitution in the nucleus on the rate of oxidation of, 290
- Sidor's blend, luminescence under influence of oz. gas, 233
- Siemens, F. and H. Moissan. (See Moissan, H.)
- "Sigma," ptomaine poisoning, 23
- Silberbach, M., and R. Pasch. (See Pasch, R.)
- Silberrad, O., constitution of nitrogen iodide, 264
- metallic derivatives of nitrogen iodide, 301
- Silindet, nitrides, 274
- diffusion of helium through, 304
- Silicate and oxychloride cements, 194
- Silicon, action on water below 100°, 83
- crystalline, soluble in hydrofluoric acid, 10
- in powdered aluminium, 6
- solubility in silver, 10, 94
- in hydrofluoric acid, 94
- spectrum, grouping of lines in, 156
- Silk, artificial, 83
- Silver in same group with alkaline metals, attempt to explain, 271
- solubility of silicon in, 10, 94
- chloride, silver oxide, and solutions of chloride of potassium and potash, equilibrium of solutions between, 59
- chromates, 45
- cyanate, bromination, 253
- pyrophosphate, acid, 117
- salts, colloidal, 304
- Simmons, W. H., refractive index of clove oil, 148
- Simon, L. J., product of spontaneous alteration of oxalic acid, 35
- and A. Conduche, action of oxalic acid on aromatic aldehydes, 117
- Simonet, M., and L. Vignon. (See Vignon, L.)
- Singer, L., and A. Rosenheim. (See Rosenheim, A.)
- Sir John Cass Technical Institute, 136
- Slator, A., decomposition of ethylene iodide under influence of iodine, 291
- Sluiter, C. H., and G. A. L. de Bruyn. (See De Bruyn, C. A. L.)
- Smith, E. F., and F. F. Exner, atomic weight of tungsten, 37, 49, 66
- H. G., absence of gum and presence of a new diglucoside in skins of Eucalypts, 68
- H. P., persulphate method of estimating manganese in iron and steel, 237
- Smoke, formic aldehyde in, 45
- Society of Arts, 244
- Silver Medal, 7
- Sodium borate, physical characters of, 284, 286
- nitrate, commercial, estimation of perchlorate of sodium in, 41
- effect of long-continued use on constitution of soil, 18
- perchlorate in commercial nitrate of sodium, estimation, 41
- peroxide, use for qualitative analysis of organic substances, 46
- phenylglycidate, interaction with phenylhydrazine, 277
- salt of diacetylacetone, action of acetyl chloride on, 19
- of acetyl chloride, preparation from sodium amide, 311
- tungstates, action of zinc on, 117
- vanadate liquors, purification, 116
- Soil constitution, effect of long-continued use of sodium nitrate on, 18
- Soils, available plant food in, 265
- analysis, mechanical, 17, 80
- nitrifying power, 250
- Soils, surface flow of, 141
- Solubility, 157
- Solutions, dilute, theory of, based on van 't Hoff's law, 148
- electric conductivity in bromine, 269
- Solvents, influence on rotation of optically active compounds, 20
- Sonstadt, E., attractive force of crystal for like molecules in saturated solutions, 302
- South-Western Polytechnic, 135
- Southerfield, F., cheap Kipp's apparatus, 286
- Williamson's theory of etherification, 23
- Spectra, flame, 13
- of sun spots and stars, relation between, 59
- ultra-violet absorption of enol-ketotautomers, 19
- "Spectrum Analysis, Introduction to Study of" (review), 160
- Spectrum, absorption, of nitrosodimethylamine, 2 p
- attributed to chlorophyll, 291
- of silicon, grouping of lines in, 156
- Spinel, artificial quadratic, of rhombic anhydrite type, 35
- Springs, hot, radio-active gaseous mixture arising from, chemical composition, 328
- Stahler, A., and B. Denk, tetra-actin, 28
- Starch and flour compositions, 195
- Stark, J., "Jahrbuch der Radioaktivität und Elektronik" (review), 31
- Stars, spectra of, and sun spots, relation between, 89
- Steam at high temperature, energy of, 139
- "Steel, Carbonised, Physical and Physico-chemical Researches on," (review), 81
- "Steel, Metallurgy of" (review), 33
- Steel and steel-making alloys, determination of molybdenum in, 248
- determination of chromium in, 320
- manganese in, perchlorate method of estimating, 237
- structural, fracture under alternating stresses, 217
- Steels, carbon and other, cementation, 44
- chromium, preparation and properties, 160
- determination of sulphur in, 230
- molybdenum, properties and constitution, 232
- transition temperatures, 243
- tungsten, constitution and properties, 221
- vanadium, 148
- Stephens, plastic materials, 209
- "Stereo-chemistry, Materials of" (review), 116
- "Stereo-chemistry, Outlines of" (review), 268
- Stewart and Corbin's Handbook on Physics and Chemistry, 24
- Stilbene, action of chromyl chloride on, 250
- group, colouring matters of, 253, 254
- Stokes, G. J., new theory of the periodic law, 159
- Stromberg, detection, microchemical, 305
- chromate, properties of, 305
- Styrene, action of chromyl chloride on, 250
- Suckert, L., and W. J. Muller. (See Muller, W. J.)
- Sudborough, J. J., influence of radium radiations on labile stereo-isomerics, 31
- and H. H. Abbott, differentiation of primary, secondary, and tertiary amines, 31
- and S. H. Beard, additive compounds of anhydrous magnesium bromide with organic oxygen and nitrogen compounds, 21
- Sugar from aorb berries, 304
- Sugars, reducing, separation and isolation by means of hydrate, 293
- Sulphamide preparation, 161
- Sulphate, ferrous, use in estimation of chlorates and bromates, 195
- titaneous, electrolytic preparation, 278
- Sulphonphenylalkylamines, 278
- Sulphonphenylchloroamides, 32
- Sulphonylchloroamides, 32
- Sulpho-organic compounds, heat of combustion in, 32
- Sulphur, alkyl derivatives, 18
- and oxygen, 191
- in iron, determination of total by evolution, 326
- and steel, determination, 230
- lines in photographic spectroscopy of minerals, 140
- Sumpper, W. E., measurement of small differences of phase, 278
- Sun, newly discovered gases in, 103
- Sunlight, influence on dissolution of gold in aqueous potassium cyanide, 272
- Sunspots and stars, relation between spectra of, 89
- Swan, Sir J. W., Hughes Medal, 250, 303
- "Swiss Scientific Society, Transactions" (review), 63
- Sylvester Medal, 250
- Synthesis, asymmetric, 251
- "TABLES for Qualitative Chemical Analysis" (review), 254
- Tannin, estimation with ferrous salts, 141
- Tartaric, alkyl and potassium alkyl, in aqueous solutions, relationship between solution-volume and rotation, 20
- Tattersall, G., and D. T. Jones. (See Jones, D. T.)
- "Technical Products, Chemical Examination of" (review), 116
- Technical research and the college system, 2
- "Techniques" (review), 71
- "Telegraphy and Telephony, Elementary Lectures on" (review), 9
- Tellurium, alkyl derivatives, 18
- argon, and beryllium, atomic weights, irregularities of, 260
- place in classification of elements, 71
- radio-, 92
- Temperature, low, phenomena and their scientific applications, 141
- Tetrachlorotoluenes, constitution, 252
- Tetramethyl methylglucosides and tetramethyl glucose, stereo-isomeric, 250
- Thibault, P., bismuthoprotocatechuic acid, 244
- phthalate and mellate of bismuth, and pyrophosphoric bismuth, 148
- some compounds of bismuth with the oxygenized acids, 57
- Thiourides, cyclic, examination and synthesis, preparation of symmetric, 173
- Thomas, V., thallous nitrate and nitrite, 56
- Thompson, S. P., crystals showing the phenomenon of luminous rings, 279
- rapid method of approximate harmonic analysis, 315
- W. P., and Co., patent law, 1902, 147
- Thorium, 155, 163
- separation from cerium, lanthanum, and didymium by metanitrobenzoic acid, 196, 201
- Thornton, W. M., magniesation of iron in bulk, 22
- sensitive hygrometer, 242
- Thorpe, J. F., H. Baron, and G. P. Remley. (See Baron, H.)
- Ticbhorne, Prof., general method in qualitative analysis for determining the presence of an oxide, 33
- Tiffenau, M., synthesis of estragol and the aromatic derivatives with unsaturated chains, 181
- and A. Behal. (See Behal, A.)
- Tilden, W. A., and F. P. Leach, limonene nitrosocyanides, 21
- Tin in the carbon group, attempt to explain the occurrence of, 271
- paste, electrolytic preparation, 324
- Tinkler, C. K., and J. J. Dobbie. (See Dobbie, J. J.)
- Titberley, A. W., acylation of amides, 263
- Titration, use of tetroxalate of potassium in, 91
- Tobacco combustion, formation of formic aldehyde, 281
- Toluene, halogen derivatives, oxidation, 290
- Tommasi, D., transformation of thermochemical energy into voltaic energy or electromotive force, 41
- Tortoise, urine of, 64
- Traube, I., contribution to the theories of osmosis, solubility, and narcotics, 137
- W., and L. Hermann, 2-phenyl-hypoxanthine and 2-phenyladenine, 46
- Triazines, 83
- Treadwell, F. P., and W. T. Hall, "Applied Chemistry" (review), 116
- Tree, mandarin orange, production and distribution of organic substances in, 244
- Triarsenic, action of hydrobromic and hydrochloric acid on, 328
- Trichlorotoluene, chlorination in presence of the aluminium-mercury couple, 252
- Trill, A., solution of formic aldehyde in the combustion of tobacco, 281
- normal presence of formic aldehyde in products of combustion of smoke, 45
- Trioxides, inorganic, composition, 313
- and hydronic acid, 272, 287, 298, 311, 321
- Triphenylanthracene and derivatives, dihydride of, 70
- Triphenylcarbinol, transformation of benzophenone into, 36
- Triphenylmethane derivatives, heat of combustion, 293
- Triphenylmethyl, action of light on, 256
- heat of combustion, 293
- Tungsten and mercury separation, 26
- atomic weight, 37, 49, 66
- hexachloride, 66
- metallic, 67
- steels, constitution and properties, 221
- Twiss, D. H., and P. F. Frankland. (See Frankland, P. F.)
- UNDECYLMETHYLketone, 36
- University College, 123
- Tutorial College, 136
- Urban, G., yttric earth near to gadolinic earth, 145
- and H. Lacombe, serial order of the rare earths, 319
- Urine, detection of acetone in, 148
- of a tortoise, 64
- VALEUR, A., benzopinacene and benzopinacolone, 197
- Van 't Hoff's law, theory of dilute solutions based on, 145
- Vanadium alloys, preparation, 269

- Vanadium and chromium in solution together, volumetric estimation, 257
 extraction from lead vanadate, 269
 ores, formation in nature, 10
 steels, 148
 "Vegetable Alkaloids" (review), 41
 Viard, G., composition of the homologues of Schœnfurft's green, 117
 Vigou, L., optical activity of cellulose and its nitrated derivatives, 148
 and M. Simonet, substitution derivatives of phenyldiazoaminobenzene, 243
 "Vital Products, Chemical Synthesis of, and Inter-relations between Organic Compounds" (review), 221
 Voltmeter, electrostatic, 267
 Von Braun, J., removal of alkyl groups from secondary amines, 118
 Von der Forst, P., and H. Grossmann. (See Grossmann, H.)
 Von Schubowsky, G., and G. Bredig. (See Bredig, G.)
 Vondracek, R., and E. Votocek. (See Votocek, E.)
 Voss, F., and C. Paal. (See Paal, C.)
 Votocek, E., antipodal isomerism of rhodose and fucose, 304
 and R. Vondracek, separation and isolation of reducing sugars by means of hydr-zinc, 293
 Vournasos, M., detection of acetone in urine, 148
WADE, J., and H. Finnemore, influence of moist alcohol and ethylchloride on boiling-point of chloroform, 21
 Wahl, A., and L. Bouveault. (See Bouveault, L.)
 Walden, P., abnormal electrolysis, 329
 and M. Ventnerszwer, compounds of sulphurous acid gas with various salts, 58
 Wales, North, University College of, 124
 South and Monmouthshire, University College of, 125
 University College of, 124
 Walker, J., "Introduction to Physical Chemistry" (review), 68
 Warth, F. J., and R. C. Farmer. (See Farmer, R. C.)
 Water at high temperature, energy of, 139
 examination, bacterioscopic, report of committee appointed to consider standardisation of methods for, 127
 hard, softening, 93
 supply, London, 43, 106, 172, 201, 262, 314
 Waters, hardness of, use of a solution of oleate of potassium for determining, 55
 mineral, purification of natural, 11
 Watkins, E. L., and J. Morrow. (See Morrow, J.)
 Watson, E. R., acetylenic ketones, 252
 and S. Ruhemann. (See Ruhemann, S.)
 Watts, W. M., "Introduction to the Study of Spectrum Analysis" (review), 160
 Wax, 194
 "Waxes, Chemical Technology and Analysis of Oils, Fats, and" (review), 197
 Wedekind, E., products obtained by action of tertiary bases on acid chlorides, 182
 Weil, H., and R. Lambrecht. (See Lambrecht, R.)
 Weissberg, J., and C. Engler. (See Engler, C.)
 Weizmann, C., and S. S. Pickles. (See Pickles, S. S.)
 Werner, A., and W. Seybold, new method of converting organic acids into esters, 256
 E. A., condensation of formaldehyde with acetone, 265
 decomposition of chloralhydrate by sodium hydroxide and by certain salts, 253
 researches on chromogenic acids, 254
 Weston, F. E., "Scheme for the Detection of the more Common Classes of Carbon Compounds" (review), 268
 Wetherell, E. W., attempt to explain the irregularities of the atomic weights of beryllium, argon, and tellurium, 260
 the occurrence of zinc, cadmium, and mercury in same group with alkaline earths, &c., 271
 Wheat bran, nature of principal phosphorus compound in, 112
 Wheeler, R. V., and W. A. Bone. (See Bone, W. A.)
 Wiesbaden, chemical laboratory at, 137
 Willcock, Miss Edith Gertrude, influence of certain salts and organic substances on the oxidation of guaiacum, 275
 Williamson's theory of etherification, 23, 44
 Willows, R. S., and A. E. Garrett. (See Garrett, A. E.)
 Willstatter, R., peroxide of hydrogen of crystallisation, 59
 Winkler, L. W., use of a solution of oleate of potassium for the determination of hardness of waters, 55
 Wolff, A., and R. Wolff-nstein, quantitative determination of active oxygen in organic persulphates, 233
 L., and H. Lindenhayn, fatty aromatic diazo-amido compounds, 83
 Wolfenstein, R., and A. Wolff. (See Wolff, A.)
 Wollastonite, platinum in, 77
 Wolverhampton Municipal Science and Technical School, 137
 Wood, J., and F. R. Japp. (See Japp, F. R.)
 Wood, action on photographic plate in dark, 104
 Wool fibres, action of acid dyes on, 233
YOUNG, S., address to chemical section of British Association, 97
 Yttric earth near to gadolinium, 287
ZINC, action on sodium tungstates, 117
 and iron, separation, 215
 and magnesium alloys, 161
 and nickel, separation, 215
 electrolytic, 45
 occurrence in same group with alkaline earths, 271
 sulphide, phosphorescing, 233, 305
 Zirconium tetraiodide, 231





80637

P
Chem & Phys
C

Author Chemical News

Title

UNIVERSITY OF TORONTO
LIBRARY

Do not
remove
the card
from this
Pocket

Acme Library Card Pocket
Under Pat. "Ref. Index File."
Made by LIBRARY BUREAU

